Reactions of cyclopentadienes with phorone

N. B. Ivchenko,[a] P. V. Ivchenko,[a] I. E. Nifant'ev,[a] I. A. Kashulin,[a] I. V. Taidakov,[a] and L. G. Kuz'mina[b]*

[a]*M. V. Lomonosov Moscow State University, Department of Chemistry, Leninskie Gory, 119899 Moscow, Russian Federation. Fax: +7 (095) 939 4523. E-mail: inif@org.chem.msu.su*
[b]*N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 31 Leninsky prosp., 117907 Moscow, Russian Federation. Fax: +7 (095) 954 1279*

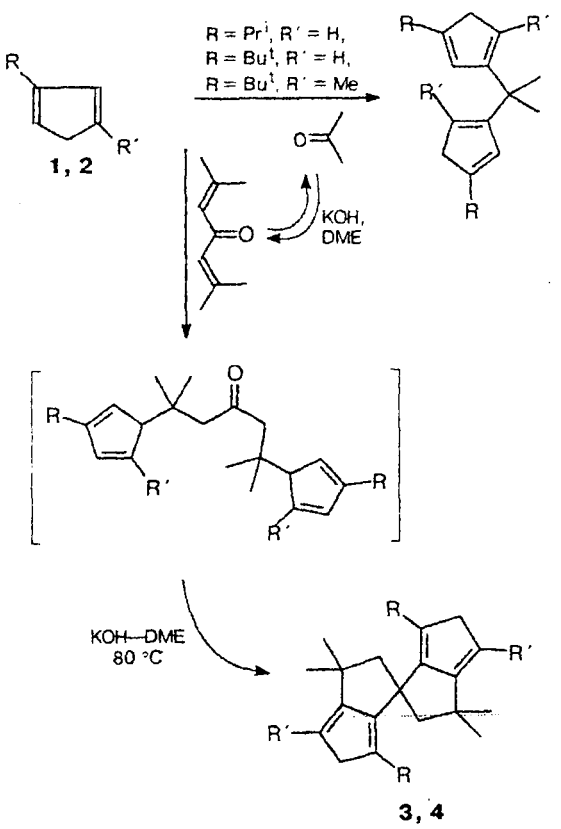
Reactions of different cyclopentadienes with phorone were studied. Nonsubstituted and monosubstituted cyclopentadienes form annelation products, *viz.*, 4,4,8,8-tetramethyl-1,3a,4,5,6,7,8,8a-octahydroazulen-6-ones.

Key words: cyclopentadienes, intermolecular cyclization, Michael addition, azulenones.

Recently,[1–3] we have studied the reactions of cyclopentadienes and indenes with carbonyl compounds in alkali—aprotic polar solvent systems. It was demonstrated that the two-phase KOH—1,2-dimethoxyethane (DME) mixture is the most efficient system. A wide range of substituted bis(cyclopentadienyl)- and bis(indenyl)methanes were prepared in satisfactory yields with the use of this system. Unexpectedly,[2] in the reactions of 1,3-dimethylcyclopentadiene (**1**) and 1-methyl-3-phenylcyclopentadiene (**2**) with acetone, spiro compounds **3** and **4**, respectively, rather than the target bis(cyclopentadienyl)methanes were formed as the major products. We suggested that under alkaline conditions, acetone undergoes partial trimerization to form phorone, which reacts with disubstituted cyclopentadienes yielding spiro compounds (Scheme 1).

To verify this suggestion, we studied the reactions of different cyclopentadienes with phorone under standard conditions (KOH—DME). The results of this investigation are reported in the present work.

Scheme 1



R = R′ = Me (**1**, **3**); R = Ph, R′ = Me (**2**, **4**)

Results and Discussion

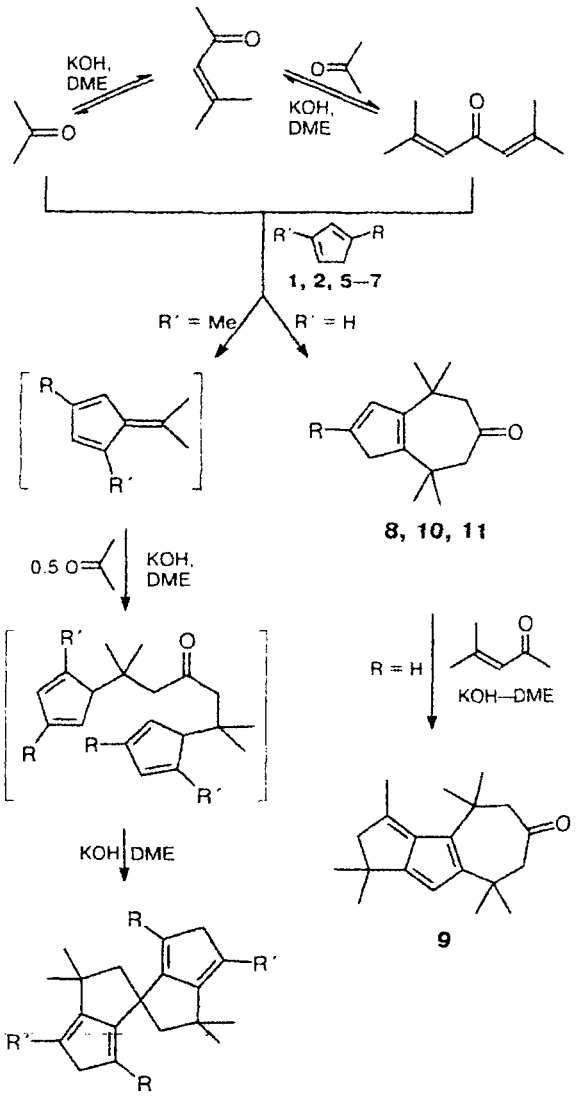
The reactions of 1,3-dimethyl- and 1-methyl-3-phenylcyclopentadiene (**1** and **2**, respectively) with phorone, like the reactions with acetone, afforded compounds **3** and **4**, respectively. The yields of these products were low, 5—10% (the yields were estimated from the analysis of the ^{1}H NMR spectra of the reaction mixtures, *viz.*, from the integrated intensities of the characteristic signals for the methylene fragments of compounds **3** and **4**).

The reactions of unsubstituted cyclopentadiene (**5**), methylcyclopentadiene (**6**), and *tert*-butylcyclopentadiene (**7**) with phorone (Scheme 2) gave ketones **8**, **10**, and

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 4, pp. 721—724, April, 2000.

11, respectively, as the major products (the yields were 20—34%). Compound **9** was obtained as a by-product in the reaction with cyclopentadiene **5**. No noticeable amounts of spiro compounds analogous to **3** and **4** were detected, because the ^{1}H NMR spectra of the reaction mixtures did not have signals characteristic of the methylene fragments of compounds **3** and **4**.

Scheme 2

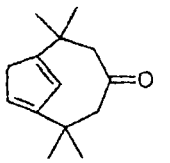


R = H (**5**, **8**); Me (**6**, **10**); Bu^t (**7**, **11**)
R′ = H (**5—7**)

Therefore, we established that the mechanism of the reactions of cyclopentadienes with acetone is more complicated than that suggested previously (see Scheme 1). In a strongly basic system (KOH—DME), acetone and phorone are rather rapidly converted into an equilibrium mixture of aldol condensation and retroaldol reaction products, *viz.*, acetone + mesityl oxide + phorone (see Scheme 2). Actually, compound **9** is a formal product of the reaction of hexahydroazulenone with mesityl oxide.

The reactions of phorone with unsubstituted and monosubstituted cyclopentadienes **5—7** proceeded rather rapidly due to the high reactivity of the latter. Partial decomposition of phorone to form acetone and mesityl oxide had no time to occur. Products **8**, **10**, and **11** were obtained in satisfactory yields, whereas the formation of bis(cyclopentadienyl)methanes was not observed. 1,3-Disubstituted cyclopentadienes **1** and **2** are more inert in the reactions with carbonyl compounds due to steric factors. As a result, the reactions of compounds **1** and **2** with both phorone and acetone afforded spiro compounds **3** and **4**, respectively, as the only products (which are the most stable compounds). In the case of 3-*tert*-butyl-1-methylcyclopentadiene,[2] the effect of steric factors is compensated to a great extent by the donor nature of the *tert*-butyl substituent as a result of which the MeBu^{t}Cp$^-$ anion that formed in this reaction is more nucleophilic than the anions of cyclopentadienes **1** and **2**. Because of this, the former readily reacts with the corresponding fulvene to give a bis(cyclopentadienyl) compound (see Scheme 1). Hexahydroazulenones cannot be formed from disubstituted cyclopentadienes due to steric factors.

The addition of unsubstituted cyclopentadiene **5** to phorone could give compound **12** as an alternative product.



12

Since the data from ^{1}H and ^{13}C NMR spectroscopy did not allow us to unambiguously choose between the reaction products (**8** or **12**), we performed X-ray diffraction study of the resulting product. It was established that the reaction actually gave compound **8**. In molecule **8** (Fig. 1), the seven-membered ring adopts a twist conformation and the cyclopentadienyl ring is planar. No noticeable deviations of the bond lengths and bond angles (Tables 1 and 2, respectively) from the expected values are observed.

Table 1. Bond lengths (d) in molecule **8**

Bond	d/Å	Bond	d/Å
O(1)—C(1)	1.221(2)	C(4)—C(5)	1.486(1)
C(1)—C(2)	1.511(2)	C(5)—C(6)	1.355(2)
C(1)—C(10)	1.511(2)	C(6)—C(7)	1.478(2)
C(2)—C(3)	1.542(2)	C(7)—C(8)	1.509(1)
C(3)—C(4)	1.522(1)	C(8)—C(9)	1.522(1)
C(3)—C(11)	1.540(2)	C(9)—C(10)	1.544(2)
C(3)—C(12)	1.547(2)	C(9)—C(13)	1.545(2)
C(4)—C(8)	1.363(1)	C(9)—C(14)	1.546(2)

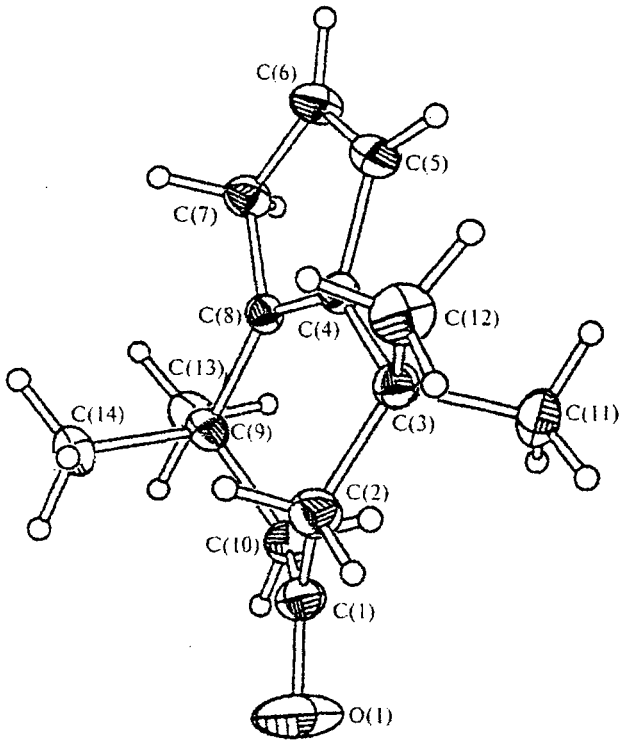


Fig. 1. Molecular structure of compound **8**.

Experimental

All experiments were carried out under argon. The ^1H and ^{13}C NMR spectra were recorded on Varian VXR-400 and Varian VXR-300 instruments. Cyclopentadiene (**5**) and methylcyclopentadiene (**6**) were freshly distilled before use. The corresponding dimers (Merck) were heated to boiling in a distillation flask equipped with a 60—70-cm long Vigreaux column (the diameter was ~2 cm) and an efficient condenser, the temperature of vapors being maintained at 40—60 °C and 60—80 °C, respectively. The distillate was collected into an ice-cooled receiver. The resulting products were dried with $MgSO_4$. 1,3-Dimethylcyclopentadiene (**1**).[4] 1-methyl-3-phenylcyclopentadiene (**2**)[5] (m.p. 58 °C, *cf.* Ref. 5: m.p. 60 °C), and *tert*-butylcyclopentadiene (**7**)[6] were synthesized according to known procedures. The ^1H NMR spectra of compounds **1**, **2**, and **7** coincide with those reported previously.[4—6]

Table 2. Bond angles (ω) in molecule **8**

Angle	ω/deg	Angle	ω/deg
O(1)—C(1)—C(2)	118.99(13)	C(6)—C(5)—C(4)	109.43(10)
O(1)—C(1)—C(10)	119.69(12)	C(5)—C(6)—C(7)	109.18(10)
C(2)—C(1)—C(10)	121.30(10)	C(6)—C(7)—C(8)	104.48(9)
C(1)—C(2)—C(3)	119.28(10)	C(4)—C(8)—C(7)	108.74(9)
C(4)—C(3)—C(11)	109.38(9)	C(4)—C(8)—C(9)	130.50(9)
C(4)—C(3)—C(2)	113.93(8)	C(7)—C(8)—C(9)	120.75(9)
C(11)—C(3)—C(2)	110.70(9)	C(8)—C(9)—C(10)	111.28(8)
C(4)—C(3)—C(12)	109.00(9)	C(8)—C(9)—C(13)	109.96(9)
C(11)—C(3)—C(12)	108.05(10)	C(10)—C(9)—C(13)	106.16(9)
C(2)—C(3)—C(12)	105.56(9)	C(8)—C(9)—C(14)	110.80(8)
C(8)—C(4)—C(5)	108.17(9)	C(10)—C(9)—C(14)	110.96(9)
C(8)—C(4)—C(3)	131.76(9)	C(13)—C(9)—C(14)	107.51(9)
C(5)—C(4)—C(3)	120.06(9)	C(1)—C(10)—C(9)	117.72(10)

Reaction of 1,3-dimethylcyclopentadiene (1) with phorone. Compound **1** (10 g, 0.106 mol) was added dropwise to a suspension of KOH (15.9 g, 0.28 mol) in DME (50 mL) at 0 °C and then cooling was discontinued. After 10 min a solution of phorone (14.7 g, 0.106 mol) in DME (15 mL) was added dropwise at ~20 °C and the reaction mixture was refluxed with stirring for 4 h and kept for ~10 h. Water (80 mL) was added followed by 10% H_3PO_4 until the reaction mixture became neutral. The products were extracted with hexane (3×100 mL) and the combined extracts were washed with water, dried with Na_2SO_4, and concentrated. Analysis of the residue (15.8 g, brown oil) by ^1H NMR spectroscopy demonstrated that the residue contained compound **3** (the spectrum of the mixture had characteristic signals of the methylene fragments of compound **3**; below are given the spectral data for the pure compound prepared according to a procedure reported previously[2]) and a mixture of unidentified products. Compound **3**, ^1H NMR ($CDCl_3$, 30 °C), δ: 1.09 and 1.11 (both s, 6 H each, $>C(C\underline{H}_3)_2$); 1.48 and 1.76 (both br.s, 6 H each, $=C(C\underline{H}_3)-$); 2.06 and 2.17 (both d, 2 H each, $>CH_2$, AB system, J_{AB} = 12.9 H); 2.87 (s, 4 H, $=C(CH_3)-C\underline{H}_2-C(CH_3)=$).

Reaction of 1-methyl-3-phenylcyclopentadiene (2) with phorone. Analogously, dark-brown oil was obtained from compound **2** (5.5 mL, 0.035 mol) and phorone (5.7 mL, 0.035 mol) in a suspension of KOH (5.3 g, 0.094 mol) in DME (30 mL) in a yield of 7.3 g. Analysis of this mixture by ^1H NMR spectroscopy demonstrated that it contained compound **4** (the spectrum of the mixture had characteristic signals of the methylene fragments of compound **4**; below are given the spectral data for the pure compound prepared according to a procedure reported previously[2]) and a mixture of unidentified products. Compound **4**, ^1H NMR ($CDCl_3$, 30 °C), δ: 1.33 and 1.37 (both s, 6 H each, $>C(CH_3)_2$); 2.10 and 2.65 (both s, 6 H each, $=C(C\underline{H}_3)-$); 2.39 and 2.65 (both d, 2 H each, $=CMe-C\underline{H}_2-$, AB system, J_{AB} = 14.4 Hz); 3.49 and 3.58 (both s, 2 H each, $-CMe_2-C\underline{H}_2-$, AB system, J_{AB} = 21.2 Hz); 6.93—7.13 (m, 10 H, Ph).

4,4,8,8-Tetramethyl-1,4,5,6,7,8-hexahydroazulen-6-one (8) and 1,3,3,5,5,9,9-heptamethyl-3,5,6,7,8,9-hexahydro-2*H*-cyclopenta[*a*]azulen-6-one (9). Analogously, the reaction of cyclopentadiene (19.7 mL, 0.24 mol) and phorone (22 g, 0.16 mol) in a KOH suspension (23.9 g, 0.43 mol) in DME (200 mL) afforded (after vacuum distillation) light-orange crystalline compound **8** and red-brown crystalline compound **9** in yields of 7.28 g (22.4%, b.p. 73—85 °C (0.1 Torr)) and 3.63 g (16%, b.p. 100—130 °C (0.1 Torr)), respectively.

Compound 8: m.p. 74—76 °C. Found (%): C, 82.22; H, 9.92. $C_{14}H_{20}O$. Calculated (%): C, 82.30; H, 9.87. ^1H NMR ($CDCl_3$, 30 °C), δ: 1.26, 1.27 (both s, 6 H each, $-CMe_2-$); 2.64 and 2.74 (both s, 2 H each, $-CH_2-$, AB system, J_{AB} = 20.2 Hz); 3.11 (dd, X_2, 2 H, $-C\underline{H}_2-$); 6.29 (dt, M, 1 H, $-CH=$); 6.54 (dt, A, 1 H, $-CH=$) (AMX_2 of the five-membered ring, J_{AX} = J_{MX} = 1.5 Hz, J_{AM} = 5.5 Hz). ^{13}C NMR ($CDCl_3$, 30 °C), δ: 30.4 and 31.4 ($-CH_3$); 34.1 and 34.4 (>C<); 43.2 (CH_2 of the five-membered ring); 57.2 and 57.8 (CH_2); 129.6 and 133.9 (—CH=); 144.9 and 145.6 (>C=); 211.4 (>C=O).

Compound 9: m.p. 113—114 °C. Found (%): C, 84.42; H, 9.89. $C_{20}H_{28}O$. Calculated (%): C, 84.45; H, 9.92. ^1H NMR ($CDCl_3$, 30 °C), δ: 1.24, 1.30, and 1.37 (all s, 6 H each, $-CMe_2-$); 2.45 (s, 3 H, CH_3); 2.65, 2.75, and 2.84 (all s, 2 H each, $-CH_2-$); 5.77 (s, 1 H, —CH=). ^{13}C NMR ($CDCl_3$, 30 °C), δ: 29.2, 30.6, and 31.1 (CH_3); 34.5, 34.8, and 35.5 (>C<); 62.8, 59.2, and 57.1 (CH_2); 111.7 (—CH=); 128.9, 145.0, 149.6, 154.4, and 159.6 (>C=); 212.3 (C=O).

Table 3. Details of X-ray diffraction analysis of compound **8**

Parameter	Value
Molecular formula	$C_{14}H_{20}O$
Molecular weight	204.30
Color of the crystal	Light-yellow
Crystal habitus	Parallelepiped
Crystal dimensions, mm	0.62×0.38×0.34
ρ_{calc}/g cm^{-3}	1.138
Diffractometer	"Siemens SMART"
T/K	150.0(2)
Radiation (λ/Å)	Mo-Kα (0.71073)
Scanning technique	ω
Scan step, ω/deg	0.3
Time per scan step, t/s	15
Number of measured reflections	9242
Number of independent reflections	3144 (R_{int} = 0.0299)
Absorption correction	No
Method of solution	Direct
Method of refinement	Full-matrix least-squares based on F^2
Location of hydrogen atoms	From the difference Fourier synthesis, refined isotropically
Final R factor ($I > 2\sigma(I)$)	R_1 = 0.0447, wR_2 = 0.1122
R factor based on all reflections	R_1 = 0.0523, wR_2 = 0.128

2,4,4,8,8-Pentamethyl-1,4,5,6,7,8-hexahydroazulen-6-one (10). Compound **10** was prepared analogously to **8** from methylcyclopentadiene (**6**) (20 mL, 0.2 mol) and phorone (20.7 g, 0.15 mol) in DME (200 mL) in the presence of KOH (30 g, 0.54 mol) as an orange oil. The yield was 11.2 g (25.7%), b.p. 73—85 °C (0.1 Torr). Found (%): C, 82.60; H, 10.10. $C_{15}H_{22}O$. Calculated (%): C, 82.52; H, 10.16. ^{1}H NMR ($CDCl_3$, 30 °C), δ: 1.20 and 1.22 (both s, 6 H each, $-CMe_2-$); 2.00 (s, 3 H, CH_3); 2.62, 2.67, and 2.97 (all s, 2 H each, $-CH_2-$); 6.09 (s, 1 H, $-CH=$). ^{13}C NMR ($CDCl_3$, 30 °C), δ: 30.3 and 31.4 ($>CMe_2$); 34.2 and 34.4 (>C<); 46.5, 57.3, 57.4, and 57.9 ($-CH_2-$ and $=C-CH_3$); 128.8 ($-CH=$); 140.9, 142.8, and 145.0 (>C=); 211.7 (C=O).

2-*tert*-Butyl-4,4,8,8-tetramethyl-1,4,5,6,7,8-hexahydroazulen-6-one (11). Compound **11** was prepared analogously to **8** from *tert*-butylcyclopentadiene (14.6 mL, 0.12 mol) and phorone (16.5 g, 0.12 mol) in DME (100 mL) in the presence of KOH (18 g, 0.32 mol) as an orange crystalline compound. The yield was 10.36 g (33.5%), b.p. 97—100 °C (0.1 Torr), b.p. 56—57 °C. Found (%): C, 82.94; H, 10.76. $C_{18}H_{28}O$. Calculated (%): C, 83.02; H, 10.84. ^{1}H NMR ($CDCl_3$, 30 °C), δ: 1.14 (s, 9 H, CMe_3); 1.20 and 1.21 (both s, 6 H each, $-CMe_2-$); 2.59, 2.64, and 2.98 (all s, 2 H each, $-CH_2-$); 6.04 (s, 1 H, $-CH=$). ^{13}C NMR ($CDCl_3$, 30 °C), δ: 30.3, 30.7, and 31.4 (CH_3); 32.9, 34.2, and 34.4 (>C<); 41.5 (CH_2 of the five-membered ring); 57.4 and 57.9 ($-CH_2-$); 124.9 ($-CH=$); 142.3, 144.3, and 155.0 (>C=); 211.8 (C=O).

X-Ray diffraction study of compound 8. Crystals of compound **8** suitable for X-ray diffraction study were grown by slow cooling of a solution of **8** in hexane saturated at 50 °C. The details of X-ray diffraction analysis are given in Table 3. The data were processed with the use of the SHELX-76[7] and SHELX-93[8] program packages. The molecular structure was drawn with the use of the ORTEP program. The unit cell parameters are as follows: the monoclinic system (the symmetry group $P2(1)/n$), a = 8.2759(1) Å, b = 12.9883(5) Å, c = 11.6831(1) Å, β = 108.2779(2)°, Z = 4, V = 1192.45 Å^3. The molecular structure of compound **8** is shown in Fig. 1. The bond lengths and bond angles are given in Tables 1 and 2, respectively. The atomic coordinates were deposited with the Cambridge Structural Database.

This work was partially supported by the President of the Russian Federation (the Program "Young Doctors," Project No. 96-15-969997).

References

1. I. E. Nifant'ev, P. V. Ivchenko, and M. V. Borzov, *Metalloorg. Khim.*, 1992, 5, 1371 [*Organomet. Chem. USSR*, 1992, 5 (Engl. Transl.)].
2. L. G. Kuz'mina, Yu. N. Luzikov, A. A. Sitnikov, and O. E. Sizan, *Synthesis*, 1997, 469.
3. I. E. Nifant'ev and P. V. Ivchenko, *Organometallics*, 1997, **16**, 713.
4. H. Yamazaki, T. Mise, and S. Miya, *Chem. Lett.*, 1989, 1853.
5. P. Burger, K. Hortmann, J. Diebold, and H.-H. Brintzinger, *J. Organomet. Chem.*, 1991, **417**, 9.
6. C. G. Viner and E. W. Casserli, *J. Am. Chem. Soc.*, 1990, **112**, 2808.
7. G. M. Scheldrick, *SHELXL-76, Program for Crystal Structure Determination*, University of Cambridge, Cambridge, England, 1976.
8. G. M. Scheldrick, *SHELXL-93, Program for the Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, 1993.

Received March 11, 1999;
in revised form November 18, 1999