provement in the quantum conversion efficiency for electron transfer from proflavin to $TiO_2$. The association of the dye with $\beta$-CD involves the uptake of the dye monomer into the CD cavity. The association constant $K_a$ of proflavin with $\beta$-CD at pH 1.8 was determined spectrophotometrically to be 550 ± 60 $M^{-1}$, corresponding to the reaction

$$\text{dye} + \beta\text{-CD} \overset{K_a}{\rightleftharpoons} [\text{dye}\cdots\beta\text{-CD}] \qquad (1)$$

Further evidence that the association of proflavin with $\beta$-CD improves the efficiency of electron injection from the dye molecule to $TiO_2$ came from studies involving *N*-octylpyridinium bromide, $C_8PyBr$. The *N*-octylpyridinium cation ($C_8Py^+$) has a high association constant ($K_a = 870 \pm 120\ M^{-1}$) for $\beta$-CD and is expected to impede the diffusion of proflavin into the CD cavity. Curves c-e of Figure 1 show that as the concentration of $C_8Py^+$ increases, the yield and rate of $H_2$ production decrease, indicating a decline in the quantum conversion efficiency for charge transfer from the excited state of proflavin to $TiO_2$. At the highest concentration of $C_8Py^+$ ($8.8 \times 10^{-2}$ M), the rate of $H_2$ production was comparable to that of the Pt–$TiO_2$–PVA system. Addition of $C_8Py^+$ to the Pt–$TiO_2$–PVA system had no effect on the rate of $H_2$ evolution, suggesting that $C_8Py^+$ blocked the inclusion of the dye molecule into the cavity of $\beta$-CD. These studies clearly imply that the photosensitization efficiency for charge injection from proflavin to $TiO_2$ is improved by the association of the dye monomer with the $\beta$-CD receptor on the surface of the semiconductor particles.

In conclusion, the utility of $\beta$-cyclodextrin for enhancing dye sensitization of semiconductors has been demonstrated. The $\beta$-cyclodextrin molecule offers a unique microenvironment for augmenting the number of surface sites for dye-semiconductor interaction and for promoting charge injection from photoexcited dye molecules to the semiconductor. Further characterization of cyclodextrin complexes with other dye systems is in progress.

**Acknowledgment.** This work was supported by Contract No. 5083-260-0796 from the Gas Research Institute.

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# Cyclizations of Ene Radicals. Imidoyl Radicals as Intermediates in the Synthesis of Heterocyclic Compounds

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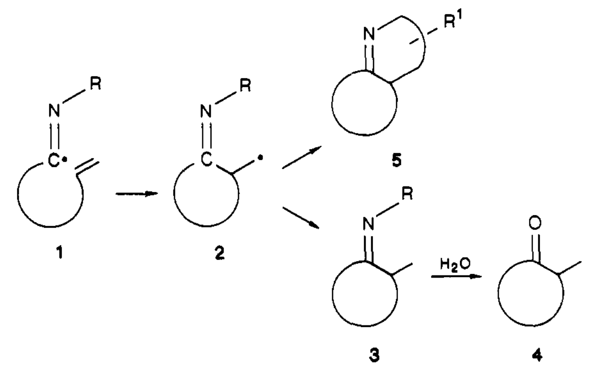
*Received October 28, 1988*

The construction of cyclic systems through the intramolecular addition of carbon centered free radicals to carbon–carbon multiple bonds is well documented.[1] A convenient method for the site-specific generation of carbon-centered free radicals involves the chemospecific homolysis of a C–halogen, C–S, or C–Se bond by trialkyltin radicals generated from the corresponding tin hydrides.[2] The tin hydride induced free radical cyclizations are not restricted to alkyl radical intermediates. Stork has introduced[3] the use of vinyl radicals in synthesis and we have shown[4] that alkoxycarbonyl radicals are excellent intermediates in a general synthesis of $\alpha$-alkylidene-$\gamma$-lactones. These results[5] prompted us to investigate the potential that other carbon-centered ene radicals, isoelectronic with vinyl and carbonyl radicals, may have as intermediates in the synthesis of functionalized cyclic compounds. Herein we report on preliminary results that illustrate the employment of imidoyl radicals, as intermediates in the synthesis of cyclic ketones and polyheterocyclic compounds.

**Scheme I**



This new method for ring formation is based on the tri-*n*-butyltin hydride (TBTH) induced generation of the imidoyl radical, followed by its intramolecular addition to a suitably positioned double bond as outlined in Scheme I.[6] We reasoned that imidoyl radicals of type **1** may cyclize to radicals **2**, which carry an exocyclic imine group. Direct hydrogen transfer to **2** would give an imine **3** that could be hydrolized to a cyclic ketone **4**. In this transformation the imidoyl radical performs as a synthetic equivalent to the carbonyl radical. However, if the R moiety in **2** would bear a radical trapping functionality a second cyclization, to a compound of type **5**, may occur. The following preliminary results (Schemes II–IV) prove the validity of these hypotheses. As starting materials we used the selenoimidates **6**, **11**, and **12** and the thioamides **18** and **20**.[7] Under standard conditions starting material (1 mmol), TBTH (1.15 mmol), and AIBN (0.15 mmol) were heated (110 °C) in dry degased toluene for 3–6 h (t.l.c.).

Treatment of selenoimidate **6** with TBTH under standard conditions followed by aqueous workup afforded nitrile **8** (50%) and chromanone **10** (50%) (Scheme II). Although the generation of imidoyl radical **7** is quantitative cyclization to imine **9** is accompanied by fragmentation into nitrile **8** and benzyl radical. When the benzyl group of the starting material was substituted by a lower alkyl group only chromanone **10** was obtained. A different reaction course was observed when *N*-aryl selenoimidates were used. Thus, *N*-tolyl derivative **11** afforded a polycyclic compound **15** (R = Ph).[8] Oxidation by DDQ resulted in the loss of two hydrogen atoms and the formation of chromanoquinoline **16** (84% from **11**). Similarly compound **12** was converted into

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[1] Reviews: (a) Surzur, J.-M. In *Reactive Intermediates*; Abramovitch, A. R., Ed.; Plenum Press: New York, 1982; Vol. 2, p 121. (b) Hart, D. J. *Science* **1984**, *223*, 883. (c) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds*; Pergamon Press: Oxford, 1986. (d) Ramaiah, M. *Tetrahedron* **1987**, *43*, 3541. (e) Curran, D. P. *Synthesis* **1988**, *417*, 489.

[2] Neumann, W. P. *Synthesis* **1987**, 665.

[3] Stork, G.; Baine, N. H. *J. Am. Chem. Soc.* **1982**, *104*, 2321. Stork, G.; Mook, R. *J. Am. Chem. Soc.* **1987**, *109*, 2829 and references cited therein.

[4] Bachi, M. D.; Bosch, E, *Tetrahedron Lett.* **1986**, *27*, 641.

[5] For additional recent examples see: (a) Marinov, N. N.; Ramanathan, H. *Tetrahedron Lett.* **1983**, *24*, 1871. (b) Padwa, A.; Nimmesgern, H.; Wong, G. S. K. *J. Org. Chem.* **1985**, *50*, 5620. (c) Hanessian, S.; Beaulieu, P.; Dube, D. *Tetrahedron Lett.* **1986**, *27*, 5071. (d) Urabe, H.; Kuwazima, I. *Tetrahedron Lett.* **1986**, *27*, 1355. (e) Beckwith, A. J. L.; O'Shea, D. M. *Tetrahedron Lett.* **1986**, *27*, 4525. (f) Knight, J.; Parsons, P. J.; Southgate, R. *J. Chem. Soc., Chem. Commun.* **1986**, 78. (g) Delduc, P.; Tailhan, C.; Zard, S. Z. *J. Chem. Soc., Chem. Commun.* **1988**, 308. (h) Crich, D.; Forth, S. M. *Tetrahedron Lett.* **1988**, *29*, 2585. (i) Boger, D. L.; Robarge, K. D. *J. Org. Chem.* **1988**, *53*, 3377. (j) Coveney, D. J.; Patel, V. F.; Pattenden, E. *Tetrahedron Lett.* **1987**, *28*, 5949. (k) Bachi, M. D.; Bosch, E. *Heterocycles*, in press. (l) Bachi, M. D.; Denenmark, D. *Heterocycles*, in press.

[6] For different reactions involving imidoyl radical intermediates see: (a) Barton, D. H. R.; Bringmann, G.; Lamotte, G.; Motherwell, B.; Motherwell, R. S. H.; Porter, A. E. A. *J. Chem. Soc., Perkin. Trans. 1* **1980**, 2657. (b) John, D. I.; Tyrrel, N. D.; Thomas, E. J. *J. Chem. Soc., Chem. Commun.* **1981**, 901. (c) Leardini, R.; Nanni, D.; Pedulli, G. F.; Tundo, A.; Zanardi, G. *J. Chem. Soc., Perkin. Trans. 1* **1986**, 1591. (d) Wirth, T.; Ruchardt, W. C. *Chimia* **1988**, *42*, 230.

[7] All compounds gave analytical data consistent with the assigned structures.

[8] For completion this reaction required 1.6 equiv of TBTH and 0.8 equiv of AIBN, and heating for 12 h.

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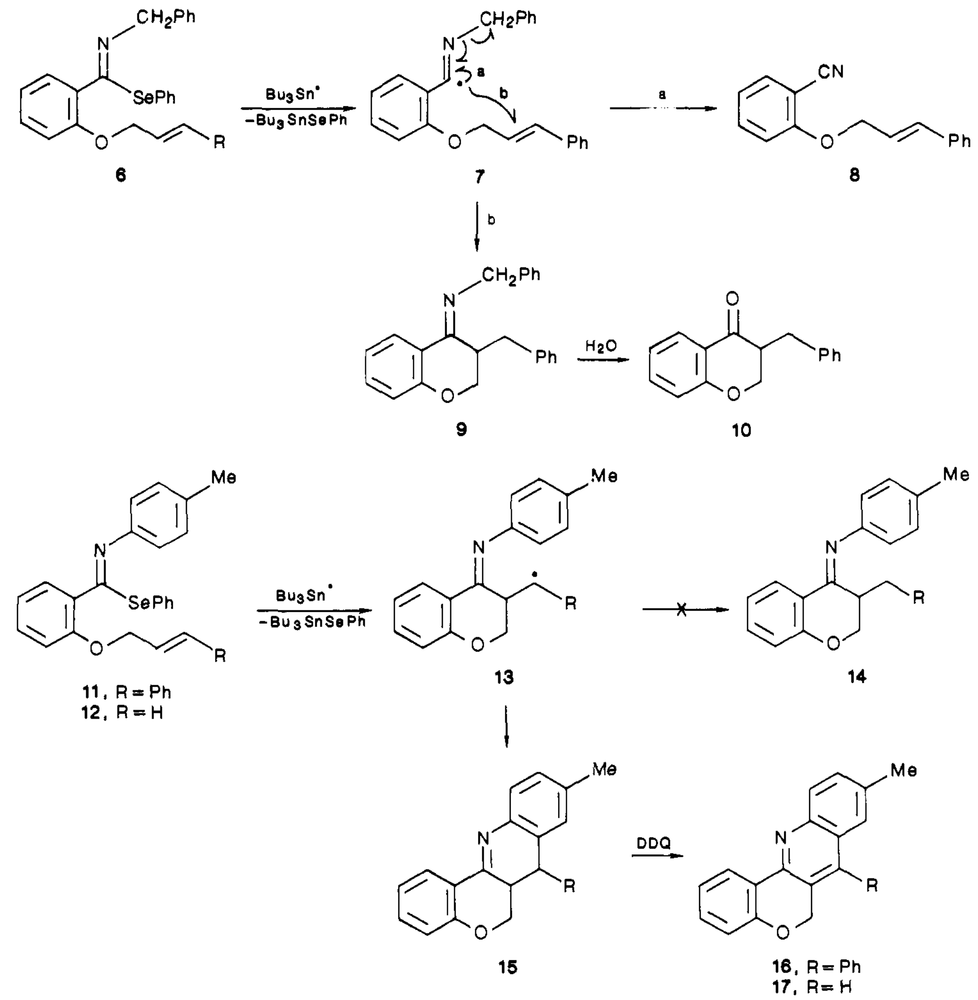
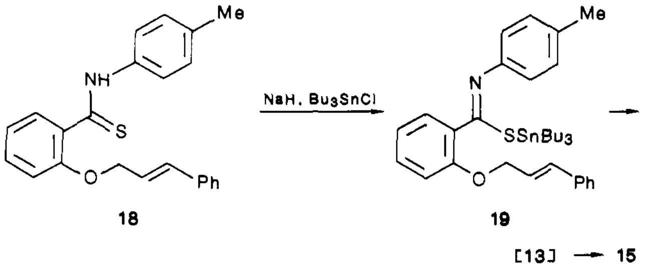
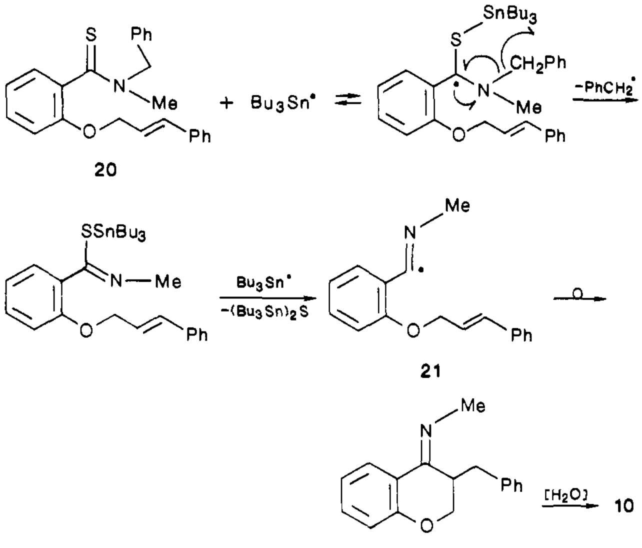
Scheme II



Scheme III



Scheme IV



chromanoquinoline **17** (86%). The adduct radicals **13** undergo a second cyclization through substitution on the juxtapositioned aromatic ring rather then hydrogen abstraction, which would have led to an imine **14** and eventually to chromanone **10**.

The use of thioimidate in lieu of selenoimidates as precursors to imidoyl radicals required the labilization of the carbon–sulfur bond. This was readily achieved by using trialkyltin thioimidates rather then aryl or alkylthioimidates.[9] Thus tri-*n*-butyltin thioimidate **19**, obtained from thioamide **18**, sodium hydride, and tri-*n*-butyltin chloride, was converted into **15** (73% from **18**) by the same method as selenoimidate **11** (Scheme III). The ready elimination of benzyl radicals resulting in the formation of nitrile **8** from imidoyl radical **7** led us to conceive an alternative method for generating imidoyl radicals which is based on a double elimination process of *N*-benzyl(*N*-alkyl)thioamides. This is illustrated in Scheme IV for the cyclization of thioamide **20** (using 2 equiv of TBTH under standard conditions) to chromanone **10** (60%), through the intermediacy of imidoyl radical **21**.

In summary, the ring closure of imidoyl radicals constitutes a useful synthetic process for the preparation of functionalized cyclic compounds under mild conditions. The full scope of this methodology is under active study and will be the subject of future reports.

**Acknowledgment.** We thank the Minerva Foundation (Munich, Germany) for financial support.

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(9) Gutierrez, C. G.; Stringham, R. A.; Nitasaka, T.; Glasscock, K. C. *J. Org. Chem.* **1980**, *45*, 3393. Gutierrez, C. G.; Summerhays, L. R. *J. Org. Chem.* **1984**, *49*, 5206.

1888 *J. Am. Chem. Soc.* **1989**, *111*, 1888-1889

**Registry No. 6**, 118630-65-2; **7**, 118630-66-3; **8**, 118655-60-0; **10**, 50684-40-7; **11**, 118655-61-1; **12**, 118630-67-4; **13** (R = Ph), 118630-68-5; **13** (R = H), 118630-69-6; **15** (R = Ph), 118630-70-9; **15** (R = H), 118630-71-0; **16**, 118630-72-1; **17**, 65038-76-8; **18**, 118655-62-2; **19**, 118630-73-2; **20**, 118630-74-3; **21**, 118630-75-4; $Bu_3SnH$, 688-73-3.

## Oxygenation of Digermene Derivatives

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We report herein that tetrakis(2,6-diethylphenyl)digermene (**1**)[1] and tetrakis(2,6-diisopropylphenyl)digermene (**1a**)[2] undergo oxygenation through several discrete pathways to provide the corresponding 1,2-digermadioxetane (**2**, **2a**), 1,3-cyclodigermoxane (**3**, **3a**), and digermoxirane (**4**, **4a**) derivatives, as shown in Scheme I. These derivatives represent three hitherto unknown ring systems, and the crystal structures of **2** and **3** are disclosed. Scheme I is analogous in several ways to that for oxygenation pathways of disilene derivatives,[3] but significant differences are also noted between the germanium and silicon series.

Exposure of **1** in toluene to dioxygen at −78 °C or 20 °C provided **2**[4] quantitatively, which upon heating at 90 °C was isomerized to **5** (see below for its structural determination). Photolysis of **2** took an entirely different course to afford **3**. The thermal and photochemical behavior of **2** contrasts with that of **6**, one of the low-temperature (−78 °C) oxygenation products of the stable disilene RR′Si=SiRR′ (R = mesityl, R′ = *tert*-butyl).[3a] Compound **6**[5] undergoes *thermal* rearrangement at 0 °C or above to provide **7** quantitatively. The crystal structure of **3** is compared below with that of **7** which has demonstrated a unique structural feature.[3a,b]

Compound **3** was also obtained directly and quantitatively from **1** with an excess of dimethyl sulfoxide or *N*-methylmorpholine-*N*-oxide in toluene at room temperature. Treatment of **1** with nitrous oxide effected a [2 + 3] addition to provide **4** upon loss of $N_2$. Since conversion of **4** into **3** with DMSO proceeded very rapidly as compared with that of **1** into **3** effected by the same reagent, **4** appears to be a likely intermediate in this latter conversion.

The majority of the above oxygenation experiments with **1** have been duplicated with **1a** as shown in Scheme I. An exception was conversion of **1a** to **3a** which was too slow to be observed.

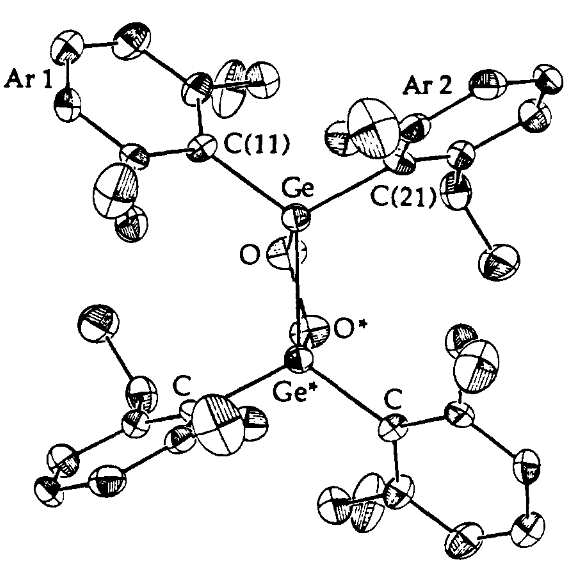
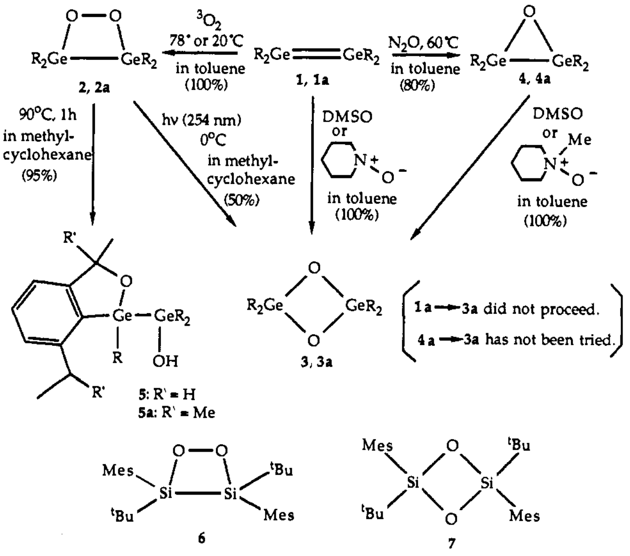


**Figure 1.** ORTEP diagram of **2**. Selected bond distances and angles are as follows: Ge–Ge* 2.441 (2) Å; O–O* 1.47 (1) Å; O–Ge = O*–Ge* 1.857 (5) Å; Ge–C(11) 1.958 (6) Å; Ge–C(21) 1.970 (7) Å; O–Ge–Ge* 74.1 (1)°; O*–O–Ge 103.9 (2)°; O–Ge–C(11) 102.8 (2)°; O–Ge–C(21) 115.0 (3)°.

**Scheme I.** Oxygenation of **1** and **1a**[a]



[a] R = 2,6-diethylphenyl for **1–5** and R = 2,6-diisopropylphenyl for **1a–5a**. The yields indicated are those for the **1** series.

Compound **5a**, the thermolysis product of **2a**, has been crystallographically identified as shown,[6] and by analogy the corresponding structure is assigned to **5** (see above).

**Crystallographic Analysis of 2.**[4,7] Compound **2** crystallizes as a discrete molecular unit with space group imposed 2-fold symmetry, and the $C_2$ axis bisects both the Ge–Ge and O–O bonds. Selected bond lengths and angles are shown in Figure 1. The central $Ge_2O_2$ trapezoidal core deviates significantly from planarity as is evident from the Ge–O–O*–Ge* torsion angle of 19.5°. The Ge–Ge* bond length is slightly shorter than normal Ge–Ge bond

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(1) (a) Snow, J. T.; Murakami, S.; Masamune, S.; Williams, D. J. *Tetrahedron Lett.* **1984**, *25*, 4191. (b) Also, see: Masamune, S.; Hanzawa, Y.; Williams, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 6136. (c) Batcheller, S. A.; Masamune, S. *Tetrahedron Lett.* **1988**, *29*, 3383. (d) Ando, W.; Tsumuraya, T. *Ibid.* **1986**, *27*, 3251. (e) For a review, see: Masamune, S. In *Silicon Chemistry*, Corey, E. R., Corey, J. Y., Gaspar, P. P. Eds.; Ellis Horwood Ltd.: New York, 1988; Chapter 25.

(2) The synthesis of **1a** will be published elsewhere.

(3) (a) Michalczyk, M. J.; West, R.; Michl, J. *J. Chem. Soc., Chem. Commun.* **1984**, 1525. (b) Michalczyk, M. J.; Fink, M. J.; Haller, K. J.; West, R.; Michl, J. *Organometallics* **1986**, *5*, 531. (c) Yokelson, H. B.; Mellevolte, A. J.; Adams, B. R.; West, R. *J. Am. Chem. Soc.* **1987**, *109*, 4116. (d) Yokelson, H. B.; Millevolte, A. J.; Gillette, G. R.; West, R. *Ibid.* **1987**, *109*, 6865.

(4) The physical properties of new compounds and further information on the X-ray crystal analyses of **2** and **3** are detailed in the Supplementary Material.

(5) The structural assignment of **6** as shown in Scheme I was based on its spectral data but not by crystallography. The authors (ref 3a) were cautious and are probably correct in choosing between the 1,2-disiladioxetane and disilaethylene perepoxide structures.

(6) Full information on the crystal structure of compound **5a** is available from S.M. upon request.

(7) Compound **2**: $C_{40}H_{52}O_2Ge_2$, $M = 710.0$ g/mol, monoclinic, $a = 18.883$ (8) Å, $b = 9.442$ (4) Å, $c = 21.335$ (9) Å, $\beta = 111.49$ (2)°, $V = 3539$ (4) Å$^3$, $Z = 4$, space group $I2/a$, $D_{calcd} = 1.33$ g cm$^{-1}$. Data were collected at −65 °C with Mo K$\alpha$ radiation (graphite monochromator $\lambda = 0.71069$ Å) on an Enraf-Nonius CAD-4. Total of 4482 reflections measured ($+h,+k\pm l$: $3° \leq 2\theta \leq 55°$), 4371 unique, $R_{int} = 0.057$. Data corrected for Lorentz polarization and absorption effects (transmission coefficients 0.73–1.08). Structure solved by direct methods.[8] Convergence on 2057 reflections [$I > 3.0\sigma(I)$] and 208 parameters resulted in $R = 0.059$ and $R_w = 0.062$ ($p = 0.03$).

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