Scheme II
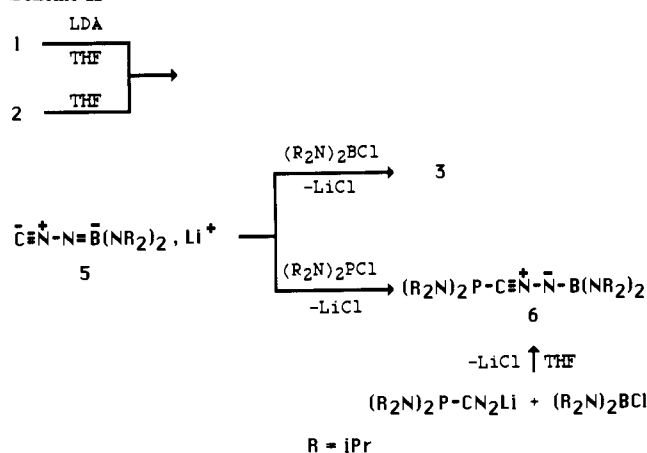

R = iPr

forded nitrilimines **3** and **4** in 85 and 80% yield, respectively. These first boranyl nitrilimines were stable enough to be purified by distillation and were unambiguously characterized by spectroscopy.[7] The isolation of **3** and **4** strongly supports the formation of lithioboranyldiazomethane **2**, since we have already shown that the lithium salts of various α-heterosubstituted diazomethanes react with bulky electrophiles at the nitrogen end, rather than at carbon, to give nitrilimines[9] (Scheme I). Whether compound **2** has a linear or slightly bent structure remains an open question as in the case of (diazomethylene)phosphoranes.[4]

Surprisingly, when the reaction of diazo **1** with LDA was carried out in THF, instead of ether, a different species (**5**), characterized by IR (2048 cm^{-1}, weak) and ^{11}B NMR (+25, broad), was obtained. Addition of bis(diisopropylamino)chloroborane to a THF solution of **5** led again to C- and N-boranyl nitrilimine **3** (80% yield), but interestingly the addition of bis(diisopropylamino)-chlorophosphane did not give rise to the C-boranyl N-phosphanyl nitrilimine **4**, but to its isomer the C-phosphanyl N-boranyl nitrilimine **6**, in 70% yield. The structure of **6** was confirmed by comparison of its spectroscopic data[7] with those of a sample prepared by reacting the lithium salt of [bis(diisopropylamino)-phosphanyl]diazomethane with bis(diisopropylamino)chloroborane (Scheme II).

The striking difference observed in the reaction of **1** with LDA, depending on the solvent, could only be rationalized by postulating the rearrangement of the first-formed species **2** into its structural isomer **5**, induced by the basicity of THF compared with that of ether. Indeed, it was possible to prepare **2** in ether and then to remove the solvent under vacuum, and the subsequent addition of THF gave rise to **5**. This rearrangement appeared to be irreversible since **5**, prepared in THF, did not isomerize into **2** in ether (Scheme II).

It is of interest to note that Hart[10] has calculated that HCNN$^-$ would be more stable than CNNH$^-$ by approximately 6 kcal/mol. These calculations also predicted that protonation of CNNH$^-$ was more likely to occur at the nitrogen atom to give isocyanamide CNNH$_2$, while protonation of HCNN$^-$ should occur at the carbon atom to give diazomethane. In other words, the proton affinity for nitrogen over carbon in CNNH$^-$ would be exactly reversed in HCNN$^-$. Since nitrilimine has been calculated[10,11] to be the least stable isomer of diazomethane, from thermodynamic and kinetic considerations the nitrilimine should never be obtained from HCNN$^-$ or CNNH$^-$. We have already shown that the use of heteroatoms such as phosphorus and silicon allows the preparation

of stable nitrilimines;[9] the results reported here demonstrate that the use of boron totally reverses the scale of kinetic behavior of diazomethane salts and greatly modifies their thermodynamic behavior.

[2 + 2] Cycloaddition of Re–Re Quadruple Bonds. Structural Characterization of the First Cyclotetrarhenium Diynes, (n-Bu4N)2Re4Cl8(μ-O)2(μ-OMe)(μ-X) (X = Cl or OMe)
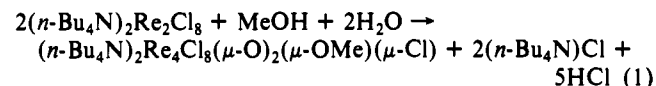
Jhy-Der Chen and F. Albert Cotton*

*Department of Chemistry and
Laboratory for Structure and Bonding
Texas A&M University, College Station, Texas 77843*

Quadruply bonded dinuclear complexes containing a Mo–Mo,[1,2] W–W,[3] or Mo–W[4] unit have been found to be able to dimerize to form rectangular clusters. A detailed report describing the preparative route for the molybdenum compounds has also been published.[5] The quadruply bonded complexes undergo [2 + 2] cycloaddition by loss of the δ components. Two single bonds are then formed to join the triply bonded dimers together.[5,6] The reactions were believed to be initiated by dissociation of phosphine ligands from the dinuclear complexes, with subsequent coupling of the coordinatively unsaturated dimer through bridging chloride.[5] Such complexes are interesting because they result from an important new type of reactivity of complexes containing metal–metal quadruple bonds. Previous efforts in this laboratory to prepare analogous rhenium compounds, i.e., four-membered Re$_4$ rings with Re–Re triple bonds and Re–Re single bonds bridged by Cl atoms, all failed. However, we have now succeeded in obtaining compounds that differ in having bridging oxygen atoms.

The complex (n-Bu$_4$N)$_2$Re$_4$Cl$_8$(μ-O)$_2$(μ-OMe)(μ-Cl) (**1**) was obtained by refluxing the quadruply bonded complex (n-Bu$_4$N)$_2$Re$_2$Cl$_8$ in MeOH and H$_2$O for 6 h.[7] The reaction proceeded according to eq 1.

$$2(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8 + \text{MeOH} + 2\text{H}_2\text{O} \rightarrow$$
$$(n\text{-Bu}_4\text{N})_2\text{Re}_4\text{Cl}_8(\mu\text{-O})_2(\mu\text{-OMe})(\mu\text{-Cl}) + 2(n\text{-Bu}_4\text{N})\text{Cl} +$$
$$5\text{HCl} \quad (1)$$

Crystals of this complex conform to the space group *Pbca* with eight molecules in the unit cell.[8]   Figure 1 shows an ORTEP

(9) (a) Castan, F.; Baceiredo, A.; Bigg, D.; Bertrand, G. *J. Org. Chem.* **1991**, *56*, 1801. (b) Sicard, G.; Baceiredo, A.; Bertrand, G. *J. Am. Chem. Soc.* **1988**, *110*, 2663. (c) Granier, M.; Baceiredo, A.; Dartiguenave, Y.; Dartiguenave, M.; Menu, M. J.; Bertrand, G. *J. Am. Chem. Soc.* **1990**, *112*, 6277. (d) Granier, M.; Baceiredo, A.; Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1350. (e) Castan, F.; Baceiredo, A.; Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1250.
(10) Hart, B. T. *Aust. J. Chem.* **1973**, *26*, 461, 477.
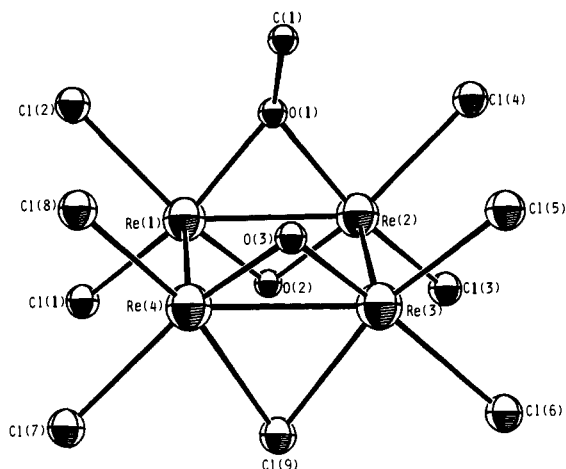(11) Moffat, J. B. *J. Mol. Struct.* **1979**, *52*, 275.

(1) McGinnis, R. N.; Ryan, T. R.; McCarley, R. E. *J. Am. Chem. Soc.* **1978**, *100*, 7900.
(2) Cotton, F. A.; Powell, G. L. *Inorg. Chem.* **1983**, *22*, 871.
(3) McCarley, R. E.; Ryan, T. R.; Torardi, C. C. In *Reactivity of Metal–Metal Bonds*; Chisholm, M. H., Ed.; ACS Symposium Series 155; American Chemical Society: Washington, DC, 1981; p 41.
(4) Carlin, R. T.; McCarley, R. E. *Inorg. Chem.* **1989**, *28*, 3432.
(5) Ryan, T. R.; McCarley, R. E. *Inorg. Chem.* **1982**, *21*, 2072.
(6) Wheeler, R. A.; Hoffmann, R. *J. Am. Chem. Soc.* **1986**, *108*, 6605.
(7) (n-Bu$_4$N)$_2$Re$_2$Cl$_8$ (0.2 g) was placed in a flask containing 40 mL of methanol and 0.05 mL of water. The mixture was heated to reflux for 6 h, resulting in a deep brown solution. The solvent was evaporated and the solid dissolved in THF. The solution was filtered, and an excess of n-hexane was added to precipitate the deep brown product. Yield: 0.06 g (35%). Crystals suitable for X-ray crystallographic analysis were obtained by layering a CH$_2$Cl$_2$/THF solution of the product with n-hexane.
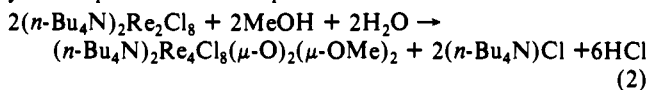
Figure 1. ORTEP drawing for $[Re_4Cl_8(\mu\text{-}O)_2(\mu\text{-}OMe)(\mu\text{-}Cl)]^{2-}$.

diagram of the anion of this molecule. The four Re atoms form two long and two short Re–Re bonds and define a rectangle. One of the long Re–Re bonds is bridged by one oxo and one methoxo group (the distance is 2.551 (1) Å), while the other is bridged by one oxo and one chloro group (the distance is 2.611 (1) Å). Each Re atom is also coordinated by two terminal Cl atoms. The Re–O–Re and Re–Cl–Re bridging angles are all acute. The ones that involve the oxo groups (85.3 (5) and 85.3 (6)°) are about 9° larger than that involving the methoxo group (76.2 (5)°). The Re–Cl–Re angle is the smallest and is about 65°. The acute angles and the Re–Re distances of 2.611 (1) and 2.551 (1) Å imply the existence of Re–Re single bonds. The Re–Re distance of the complex[11] $Re_2O_3(OMe)_6$ in which the two Re atoms are bridged by two OMe groups and one oxygen atom was found to be 2.559 (1) Å and is suggested to be consistent with the presence of a Re–Re single bond. The two short Re–Re distances, 2.261 (1) and 2.277 (1) Å, are in agreement with those known for compounds with Re–Re triple bonds. For example, the Re–Re distance of $Re_2Cl_4(dppe)_2$[12] is 2.244 (1) Å and that of $Re_2Cl_4(PEt_3)_4$[13] is 2.232 (5) Å. Thus the single bonds on the long edges and triple bonds on the short edges of the rectangle allow this Re_4 ring to be described as a metallocyclobutadiyne. The variation in the Re–O distances is as expected. Those that involve the methoxo group (2.06 (1)–2.07 (1) Å) are longer than those involving the oxo groups (1.88 (1)–1.96 (1) Å).

The complex $(n\text{-}Bu_4N)_2Re_4Cl_8(\mu\text{-}O)_2(\mu\text{-}OMe)_2$ (2) was obtained from an independent experiment.[14] The reaction was believed to proceed according to eq 2. We have been unable as yet to reproduce this compound.

$$2(n\text{-}Bu_4N)_2Re_2Cl_8 + 2MeOH + 2H_2O \rightarrow$$
$$(n\text{-}Bu_4N)_2Re_4Cl_8(\mu\text{-}O)_2(\mu\text{-}OMe)_2 + 2(n\text{-}Bu_4N)Cl + 6HCl \tag{2}$$

(8) Crystal data: space group *Pbca*, $a = 19.521$ (5) Å, $b = 36.181$ (9) Å, $c = 17.866$ (4) Å, $V = 12\,619$ (9) Å³; $Z = 8$. The diffraction data were collected at –50 °C on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα ($\lambda_\alpha = 0.710\,73$ Å) radiation. The ω collection method was used to scan a possible 12 578 data points in the range of 4° < 2θ < 50°. The structure factors were obtained after Lorentz and polarization corrections. Empirical absorption corrections based on azimuthal (ψ) scans of reflections of Eulerian angle χ near 90° were applied to the data.[9] The direct methods program in SHELXS-86[10] led to the location of the positions of the rhenium atoms. The remaining atoms were found in a series of alternating difference Fourier maps and least-squares refinements. The final residuals of the refinement were $R = 0.0616$ and $R_w = 0.0851$.

(9) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1968**, *24*, 351.

(10) Sheldrick, G. M. *SHELX-86*; Institut für Anorganische Chemie der Universität Göttingen: Göttingen, FRG, 1986.

(11) Edwards, P. G.; Wilkinson, G.; Hursthouse, M. B.; Abdul Malik, K. M. *J. Chem. Soc., Dalton Trans.* **1980**, 2467.

(12) Cotton, F. A.; Stanley, G. G.; Walton, W. A. *Inorg. Chem.* **1978**, *17*, 2099.

(13) Cotton, F. A.; Frenz, B. A.; Ebner, J. R.; Walton, R. A. *Inorg. Chem.* **1976**, *15*, 1630.

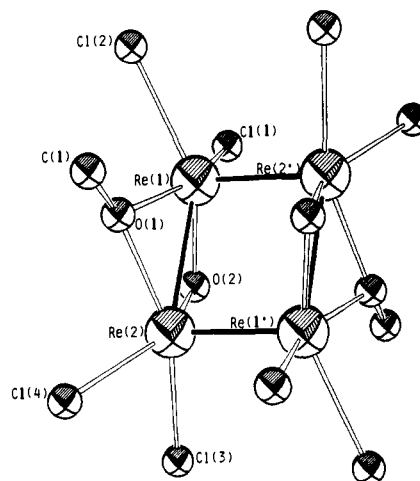(14) This product was obtained unexpectedly from a reaction of $(NBu_4)_2Re_2Cl_8$ and (+)-BINAP in boiling MeOH.

Figure 2. ORTEP drawing for $[Re_4Cl_8(\mu\text{-}O)_2(\mu\text{-}OMe)_2]^{2-}$, showing only the primary form.

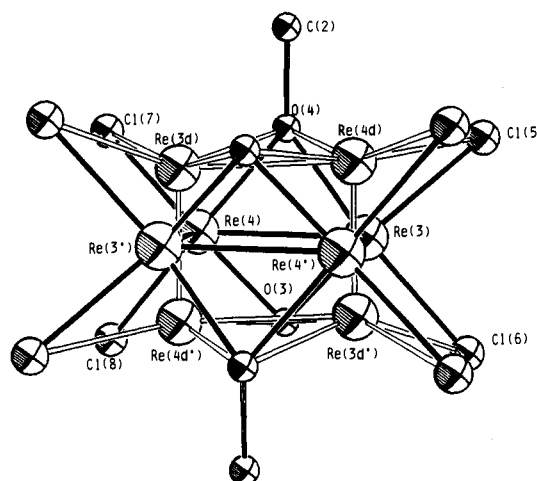**Figure 3.** ORTEP drawing for $[Re_4Cl_8(\mu\text{-}O)_2(\mu\text{-}OMe)_2]^{2-}$, showing both the primary and secondary forms.

Crystals of **2** conform to the space group $P\bar{1}$ with two independent centrosymmetric molecules in the unit cell,[15] one centered at 0, 0, 0 and the other at $^1/_2, ^1/_2, ^1/_2$. Figure 2 shows an ORTEP diagram of one of the molecules of **2**. The two long Re–Re bonds are each bridged by one oxo group and one methoxo group, and the average distance is 2.586 [2] Å. The average distance of the two short Re–Re bonds is 2.246 [2] Å. The long and short Re–Re bonds of **2** can be assigned to single and triple bonds, respectively, as in the case of **1**. The molecule of **2** has idealized C_{2h} symmetry, with the mirror plane defined by the four oxygen atoms and the 2-fold axis passing through the centers of the short Re–Re bonds.

The Re atoms of the molecule centered on $^1/_2, ^1/_2, ^1/_2$ are

(15) Crystal data: space group $P\bar{1}$, $a = 16.838$ (1) Å, $b = 17.311$ (2) Å, $c = 9.219$ (1) Å, $\alpha = 94.83$ (1)°, $\beta = 96.42$ (1)°, $\gamma = 88.28$ (1)°, $V = 2660.2$ (5) Å³, $Z = 2$. The diffraction data were collected at 20 ± 1 °C on a Rigaku AFC5R diffractometer with graphite-monochromated Cu Kα ($\lambda_\alpha = 1.54$ Å) radiation. The ω–2θ collection method was used to scan a possible 6972 data points in the range of 4° < 2θ < 130°. Absorption correction was applied to the data. The Patterson methods program in SHELXS-86[12] led to the location of the positions of the rhenium atoms. The remaining atoms were found in a series of alternating difference Fourier maps and least-squares refinements. The final residuals of the refinement without considering the disorder of the Re atoms were $R = 0.0528$ and $R_w = 0.0693$. The Re atoms of one of the two molecules solved were found to be disordered. The percentages of disorder of the principal and secondary forms calculated by the Shelx-76 program were found to be 96 and 4, respectively. The final residuals were $R = 0.048\,62$ and $R_w = 0.064\,70$. Decreasing the multiplicity of the secondary Re atoms to 3% or increasing to 5% gave R and R_w values of 0.048 70 and 0.064 81, and 0.048 81 and 0.064 74, respectively. The multiplicities of the secondary Re atoms were chosen to be 3% since they gave more reasonable thermal parameters for the Re atoms. The refinement results with different multiplicities for Re atoms are provided as supplementary material.

disordered so that while only one set of ligand atoms can be resolved, there are two incompletely occupied sets of metal atom positions. An ORTEP diagram with the two different sets of Re atoms is shown in Figure 3. It is clear that each set of four Re atoms forms a plane, and these two planes are orthogonal to each other. The primary set, Re(3) and Re(4), is 97% occupied, and the secondary set, Re(3d) and Re(4d), is only 3% occupied.

The reactions of $(n\text{-}Bu_4N)_2Re_2Cl_8$ with MeOH and H_2O are believed to be initiated by the attack of the Re^{3+} centers on the oxygen atom of methanol and/or water. The attack results in the breaking of the O–H bonds and subsequently the loss of chloride ligands from each rhenium metal center. The intermediate of low coordination number is unstable and condenses to form the tetramer, through the formation of two Re–Re single bonds that join two triple-bonded units together. The initiation is due to the high acidities of the Re^{3+} centers, which have been found to be able to rearrange the diop ligand by their coordination to the oxygen atoms of the diop ligands.[16]

Complexes **1** and **2** make an interesting comparison with $Mo_4(\mu\text{-}OMe)_2(\mu\text{-}OiPr)_2(OiPr)_8$[17] (**3**). Complex **3** has two short (2.238 (1) Å) Mo–Mo bond distances and two long (3.344 (1) Å) Mo–Mo distances, corresponding to Mo–Mo triple-bond and nonbonding distances. Complexes **1** and **2** have two triple bonds and two single bonds. The metal centers of **1** and **2** are Re^{3+} and have d^4 electronic configurations, and those of **3** are Mo^{3+} and have d^3 electronic configurations. The addition of four more electrons leads to the formation of two single bonds in both **1** and **2**.

Supplementary Material Available: Complete tables of crystal data, positional and isotropic equivalent thermal parameters, anisotropic thermal parameters, bond distances, bond angles, and refinement results for **2** with different multiplicities for Re atoms (26 pages); two listings of observed and calculated structure factors (58 pages). Ordering information is given on any current masthead page.

(16) Chen, J.-D.; Cotton, F. A. *J. Am. Chem. Soc.* **1991**, *113*, 2509.
(17) Chisholm, M. H.; Hammond, C. E.; Hampden-Smith, M.; Van Der Sluys, W. G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 904.

Novel Photodimerization of 2-Alkoxy-3-cyanopyridines Involving Unexpected Rearrangement

Masami Sakamoto,*,† Makoto Kimura,† Tsutomu Fujita,†
Takehiko Nishio,‡ Ikuo Iida,‡ and Shoji Watanabe†

*Department of Applied Chemistry, Faculty of Engineering
Chiba University, Yayoi-cho, Chiba, Japan 260
Department of Chemistry, The University of Tsukuba
Tsukuba-shi, Ibaraki, Japan 305*

A great deal of attention has been paid to the photochemistry of aromatic compounds by photochemists. Benzene and its derivatives undergo a number of important photoreactions including isomerization and photoadditions with various unsaturated compounds.[1] Pyridine undergoes fewer photochemical reactions than does benzene. It forms an unstable para-bonded isomer,[2] and

†Chiba University.
‡The University of Tsukuba.

(1) (a) McCullough, J. J. *Chem. Rev.* **1987**, *87*, 811. (b) Gilbert, A. *Synthetic Organic Photochemistry*; Horspool, W. M., Ed.; Plenum: New York, 1984. (c) Gilbert, A. *Pure Appl. Chem.* **1980**, *52*, 2669. (d) Mattay, J. *Tetrahedron* **1985**, *41*, 2405. (e) Wagner, P. J.; Nahm, K. *J. Am. Chem. Soc.* **1987**, *109*, 4404, 6528. (f) Wagner, P. J.; Sakamoto, M. *J. Am. Chem. Soc.* **1989**, *111*, 8723, 9254.

Table I. Photolysis of 2-Alkoxy-3-cyanopyridines **1a–e**

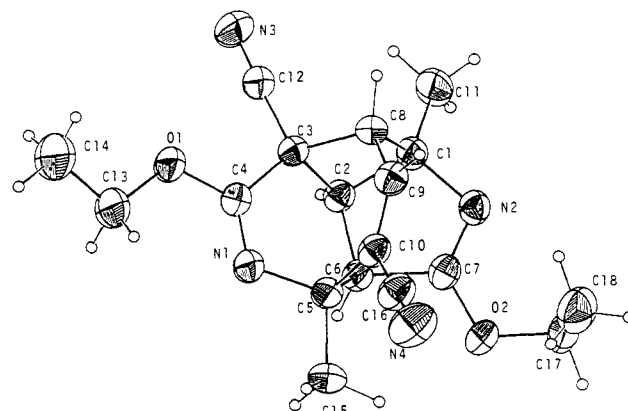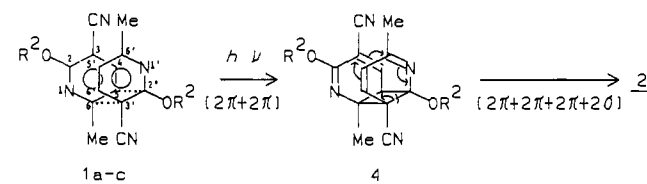| **1**	R^1	R^2	concn (mol/L)	conversn (%)	yield (%) 2	yield (%) 3
a	H	Me	0.02	52	36	44
a	H	Me	0.04	52	93	0
a	H	Me	0.20	45	93	0
b	H	Et	0.02	40	31	47
b	H	Et	0.20	40	89	0
c	H	i-Pr	0.02	44	80	trace
d	Me	Me	0.02	54	0	92
e	Me	Et	0.02	58	0	90

Figure 1. ORTEP diagram of dimer **2b**.

Scheme I

fluorinated pyridines gave azaprismanes.[3] The photoaddition of pyridines to alkenes is generally unsuccessful.[4] We now find that 2-alkoxy-3-cyano-6-methylpyridines undergo [2π + 2π] photodimerization followed by novel rearrangement. This reaction represents the first example of [2π + 2π] cyclodimerization in pyridine photochemistry.

All 2-alkoxy-3-cyanopyridines **1** in Table I were prepared by alkylation of the corresponding pyridones.[5] The structures of these compounds were determined on the basis of elemental analyses and the spectral data. The UV spectrum of the methoxy derivative **1a** in cyclohexane showed maxima at 231 (ε 10 100), 284 (8400), 289 (11 000), 294 (11 000), and 299 nm (9200).

(2) (a) Wilzbach, K. E.; Rausch, D. J. *J. Am. Chem. Soc.* **1970**, *92*, 2178. (b) Kobayashi, Y.; Ohsawa, A.; Iitaka, Y. *Tetrahedron Lett.* **1973**, 2643. (c) Chambers, R. D.; Middleton, R.; Corbally, R. P. *J. Chem. Soc., Chem. Commun.* **1975**, 731. (d) Chambers, R. D.; Middleton, R. *J. Chem. Soc., Chem. Commun.* **1977**, 154.
(3) Barlow, M. G.; Haszeldine, R. N.; Dingwall, J. G. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1542.
(4) Only a few examples have been reported. (a) Barlow, M. C. J.; Brown, D. E.; Haszeldine, R. N. *J. Chem. Soc., Chem. Commun.* **1977**, 669. (b) Saito, I.; Kanehira, K.; Shimozono, K.; Matsuura, T. *Tetrahedron Lett.* **1980**, *21*, 2737. (c) Bernardi, R.; Caronna, T.; Morrocchi, S.; Traldi, P. *Tetrahedron Lett.* **1981**, *22*, 155.
(5) (a) Hopkins, G. C.; Jonak, J. P.; Minnemeyer, H. J.; Tieckelmann, H. *J. Org. Chem.* **1967**, *32*, 4040. (b) Chung, N. M.; Tieckelmann, H. *J. Org. Chem.* **1970**, *35*, 2517.