Protonolysis of 4 and 5. A mixture of 4 (2.0 g, 0.010 mol), 1.1 g (0.010 mol) of trifluoroacetic acid, and 25 mL of dry CH_2Cl_2 was prepared at 0 °C. After 15 min, all of 4 had been converted to 5. After an additional 24 h at 25 °C, only 2,2-dimethyl-2-sila-3-pentanone (6) was present. Workup with aqueous $NaHCO_3$ followed by drying and distillation gave 1.0 g (78%) of 6,[16] bp 50–58 °C (100 mmHg), containing some minor impurities. Data for half-life determinations of the reaction of 5 with various acids were obtained in $DCCl_3$ by ^1H NMR as indicated in Table I.

Brominolysis of 4. (A) One Equivalent of Bromine. A solution of 1.89 g (0.0118 mol) of Br_2 in 50 mL of dry CH_2Cl_2 was added dropwise to a solution of 2.38 g (0.0118 mol) of 4 in 50 mL of CH_2Cl_2 at −78 °C. The flask was wrapped with aluminum foil. After addition, volatiles (which VPC indicated contained small amounts of 6) were removed by evacuation at 5 mmHg to give 2.26 g of crude product. ^1H NMR analysis showed this to consist of 78% 2,2-dimethyl-5-bromo-2-silapentan-3-one (7) and 22% 2,2-dimethyl-4,5-dibromo-2-silapentan-3-one (8). The monobromo product is quite unstable; storage of this mixture at −25 °C for 7 days resulted in the total decomposition of 7. Efforts to separate 7 from 8 by rapid chromatography, VPC, or distillation were unsuccessful. ^1H NMR of 7: δ 0.19 (s, 9 H), 3.36 (m, 4 H).

(B) Two Equivalents of Bromine. The procedure of A was followed with 2.0 g (0.010 mol) of 4 and 3.2 g (0.020 mol) of Br_2. The mixture was allowed to warm to 25 °C and stirred 30 min, whereupon the initial red color had turned to yellow. A water wash was followed by drying and distillation to give 2.5 g (87%) of 7, bp 44–50 °C (0.4 mmHg) which VPC indicated was 98% pure: ^1H NMR δ 0.31 (s, 9 H), 3.57 (dd, 1 H), 3.98 (t, 1 H), 4.82 (dd, 1 H); IR 1645, 1250, 850 cm^{-1}.

Anal. Calcd for $C_6H_{12}Br_2OSi$: C, 25.02; H, 4.20. Found: C, 25.09; H, 4.13.

(C) Three Equivalents of Bromine. The procedure of A was followed with 1.0 g (0.0050 mol) of 4 and 2.4 g (0.015 mol) of Br_2. After addition, the reaction mixture was stirred at 25 °C for 20 h. The color of the solution remained red, but titration of an aliquot with standard $Na_2S_2O_3$ solution indicated only 1.4% unreacted Br_2. The reaction mixture was washed with 0.1 N $Na_2S_2O_3$ and water, dried, and concentrated. Distillation gave 1.67 g (91%) of 4,4,5-tribromo-2,2-dimethyl-2-silapentan-3-one (9), bp 62–70 °C (0.2 mmHg), which VPC showed to be 99% pure: ^1H NMR δ 0.42 (s, 9 H), 4.23 (s, 2 H); IR 1650, 850 cm^{-1}.

Anal. Calcd for $C_6H_{11}Br_3OSi$: C, 19.64; H, 3.02. Found: C, 19.81; H, 3.13.

(D) Under Other Brominating Conditions. The use of Br_2 and pyridine, Br_2 and polyvinylpyridine, *N*-bromosuccinimide, cupric bromide, or *tert*-butyl hypobromite with 4 all afforded mixtures of 6, 7, and 8.

Preparation of Enones 10 and 11. The crude reaction mixture obtained from 2.38 g of 4 and 1.89 g of Br_2 as described above was evacuated at 5 mmHg and added to a mixture of 1.19 g (0.0118 mol) of triethylamine in 50 mL of CH_2Cl_2. After 2 h at 25 °C, the clear solution was diluted with 100 mL of pentane to form a precipitate which was removed by sintered frit filtration. Kugelrohr distillation of the concentrated filtrate gave 0.92 g (61%) of 4,4-dimethyl-4-sila-1-penten-3-one (10),[5a] bp 25 °C (5 mmHg), and 0.24 g (10%) of 2-bromo-4,4-dimethyl-4-sila-1-penten-3-one (11), bp 50 °C (0.5 mmHg): ^1H NMR (11) δ 0.30 (s, 9 H), 6.78 (s, 2 H); IR 1625, 1595, 1250, 850 cm^{-1}.

Anal. Calcd for $C_6H_{11}BrOSi$: C, 34.79; H, 5.35. Found: C, 35.03; H, 5.40.

In a completely parallel experiment, but employing 2.52 g of pure 8, short-path distillation gave 1.36 g (84%) of 11, bp 64–70 °C (8 mmHg).

Attempts at the debromination of 8 with Zn/Et_2O, $Zn/ZnBr_2/Et_2O$, $Zn/ZnBr_2/p$-dioxane (80 °C), or Ph_3P did not afford 10.

Attempted Reaction of 4 with Carbon Electrophiles. Attempted reaction of 4 with *t*-BuCl/$TiCl_4$, *t*-BuCl/Me_3SiOTf, $CH_2(OCH_3)_2/Me_3SiOTf$, or $Me_3CCHO/TiCl_4$, first at −78 °C and then at 25 °C, gave only varying amounts of protonolysis product 6. The reaction of 4 with acetyl triflate (from acetyl chloride and silver triflate in chloroform) gave only (1-acetoxycyclopropyl)-trimethylsilane: ^1H NMR δ 0.10 (s, 9 H), 0.72 (m, 4 H), 1.94 (s, 3 H); IR 3085, 1735, 1250, 1170 cm^{-1}.

Anal. Calcd for $C_8H_{16}O_2Si$: C, 55.81; H, 9.30. Found: C, 55.74; H, 9.51.

(16) Brook, A. G.; Dillon, D. J.; Pearce, P. *Can. J. Chem.* **1971**, *49*, 133.

$Mo(CO)_6$-Promoted Reductive Cleavage of the Carbon–Sulfur Bond[1]

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The hydrodesulfurization process is important in the purification of fossil fuels.[2] The commonly used catalyst for this transformation consists of molybdenum sulfide with cobalt or nickel compounds as a promoter.[3] However, the actual mode of this process is not well understood. The reaction is essentially the reductive cleavage of a carbon–sulfur bond. There are scattered examples of the use of homogeneous organometallic reagents to promote reductive cleavage of carbon–sulfur bonds. To illustrate this, metal carbonyls such as $Fe(CO)_5$,[4] $Fe_3(CO)_{12}$,[5] $Os_3(CO)_{12}$,[6] $Mn_2(CO)_{10}$,[7] and $Co_2(CO)_8$[4a,8] are effective desulfurization reagents. Recently, Alper and Blais reported that molybdenum species generated by the adsorption of $Mo(CO)_6$ on silica was an active reagent which would react with dibenzothiophene to give biphenyl.[9] No desulfurization occured when dibenzothiophene was exposed to $Mo(CO)_6$ in THF.[9] Similar reaction was observed when various thiols were treated with a preheated acetic acid solution of $Mo(CO)_6$.[10] In continuing our long time interest in the reductive cleavage of C–X bonds promoted by metal carbonyl,[11] including group VI (6)[17] metal carbonyls,[11c] we felt that $Mo(CO)_6$ itself may be able to selectively reduce other kinds of more reactive carbon sulfur bonds. We have tested this viewpoint by reacting various organosulfur compounds with $Mo(CO)_6$ and now wish to describe our results.

Results and Discussion

A THF solution of organosulfur compounds and $Mo(CO)_6$ was refluxed for 12–16 h, and after workup, the cor-

(1) Part 12 of the series "Transition-Metal Promoted Reactions". Part 11: Luh, T.-Y.; Wong, C. S. *J. Organomet. Chem.* **1985**, *287*, 231.
(2) Schuman, S. C.; Shalit, H. *Catal. Rev.* **1970**, *4*, 245.
(3) For review, see: Mitchell, P. C. H. *Catalysis* **1981**, 175.
(4) (a) Alper, H. *J. Org. Chem.* **1975**, *40*, 2694. (b) Alper, H.; Paik, H.-N. *J. Org. Chem.* **1977**, *42*, 3522. (c) Ayral-Kalonstaan, S.; Agosta, W. C. *Synth. Commun.* **1981**, *11*, 1011. (d) Daub, J.; Erhardt, G.; Jogun, K. H.; Kappler, J.; Laumer, A.; Pfiz, R.; Stezowske, J. J. *Chem. Ber.* **1982**, *115*, 1787.
(5) (a) Broadhurst, P. V.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Am. Chem. Soc.* **1981**, *103*, 3198. (b) Alper, H.; Sibtain, F.; Heveling, J. *Tetrahedron Lett.* **1983**, *24*, 5329.
(6) Adams, R. D.; Katahira, D. A.; Yang, L.-W. *Organometallics* **1982**, *1*, 235.
(7) Alper, H. *J. Organomet. Chem.* **1974**, *73*, 359.
(8) Shim, S. C.; Antebi, S.; Alper, H. *J. Org. Chem.* **1985**, *50*, 147.
(9) Alper, H.; Blais, C. *Fuel* **1980**, *59*, 670.
(10) Alper, H.; Blais, C. *J. Chem. Soc., Chem. Commun.* **1980**, 169.
(11) (a) Luh, T.-Y.; Lai, C. H.; Tam, S. W. *Tetrahedron Lett.* **1978**, 5011. (b) Luh, T.-Y.; Lai, C. H.; Lei, K. L.; Tam, S. W. *J. Org. Chem.* **1979**, *44*, 641. (c) Luh, T.-Y. *J. Organomet. Chem.* **1979**, *174*, 169. (d) Luh, T.-Y.; Lai, C. H.; Tam, S. W. *J. Chem. Soc., Perkin Trans. 1* **1980**, 444. (e) Luh, T.-Y. *Synth. Commun.* **1981**, *11*, 829. (f) Luh, T.-Y.; Lee, K. S.; Tam, S. W. *J. Organomet. Chem.* **1981**, *219*, 345. (g) Luh, T.-Y.; Lee, K. S.; Tam, S. W. *J. Organomet. Chem.* **1983**, *248*, 221.

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Table I. Desulfurization of Some Mercaptans and Thioethers with $Mo(CO)_6$

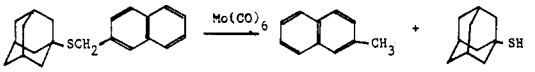
substrate	product(s)	yield, %
1-naphthalenemethanethiol (1)	1-methylnaphthalene	79
2-naphthalenemethanethiol (2)	2-methylnaphthalene	67
4-methoxybenzyl mercaptan (3)	4-methylanisol	71
4-carboxybenzyl mercaptan (4)	4-toluic acid	67
4-bromobenzyl mercaptan (5)	4-bromotoluene	63
4-chlorobenzyl mercaptan (6)	4-chlorotoluene	61
α-(thiomethoxy)acetophenone (7)	acetophenone	57
2-thionaphthol (8)	naphthalene	43
9-fluorenone thioketal 9	fluorene (13)	42
	bifluorenylidene (14)	34
1-adamantyl (2-naphthylmethyl sulfide (10)	2-methylnaphthalene	73
	1-adamantanethiol (11)	49

responding reduced products were readily obtained in moderate to good yields. The results are summarized in Table I.

As shown in Table I, benzylic mercaptans or thioethers were reduced smoothly. Functional groups such as carboxylic acid, halides, and methoxy as well as carbonyl groups remain intact under the reaction conditions. Thiomethoxy groups α to carbonyl groups can also undergo reductive cleavage under the reaction conditions. Thus, acetophenone was obtained in 57% yield from its α-thiomethoxy precursor 7.

Since the reaction was carried out in THF as described in the Experimental Section and no other possible hydrogen sources were included in the workup procedure, it is likely that the hydrogen atom in the solvent molecules was abstracted during the course of the reaction. It is known that the α-hydrogen atom in ethereal solvent molecules can be abstracted by a radical species.[11a,12] In this study, the α-hydrogen in THF should be labile and consequently, the reaction may also proceed via a radical mechanism.

Aliphatic or alicyclic thiols remain intact under the reaction conditions. Thus, more than 80% of the starting material was recovered from the reaction with 1-adamantanethiol (11). Accordingly, we felt that $Mo(CO)_6$ reagent may be able to selectively cleave the more reactive carbon–sulfur bond of a thioether. We have tested this viewpoint by studying the desulfurization reaction of 1-adamantyl 2-naphthylmethyl thioether (10) (eq 1). 2-



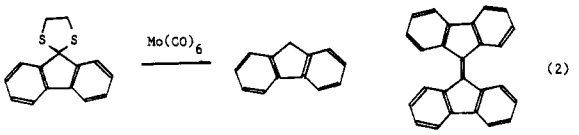
(1)

10 11

Methylnaphthalene and 1-adamantanethiol (11) were obtained in 73% and 49% yields, respectively. Thus, we believe that our reaction may be applied for removing the benzyl protective group for aliphatic or alicyclic thiols.[13]

From Table I, it is noted that the aryl–sulfur bond can also be reduced under the reaction conditions. Thus, 2-thionaphthol (8) was transformed into naphthalene in 43% yield. Similar to a previous report,[9] dibenzothiophene did not undergo desulfurization under the reaction conditions. It is noted that the aryl–sulfur bond seems to be more labile than the carbon–sulfur bond of the aliphatic analogue in the metal-catalyzed carbon–sulfur bond reductive cleavage reactions.[6]

We have also carried out the desulfurization reaction of 9-fluorenone thioketal with $Mo(CO)_6$. A mixture of fluorene (13) and bifluorenylidene (14) was obtained in 42% and 34% yields, respectively (eq 2). The isolation



(2)

9 13 14

of the latter product (14) is somewhat interesting. This may be the first example of transforming a thioketal moiety into a dimer. Previous example has suggested that the thioketone was treated with $Co_2(CO)_8$[4b,8] to give the dimer olefin. Presumably this latter reaction may occur via a carbenoid intermediate. Indeed, when thiocarbonate was treated with $Fe(CO)_5$, an iron–carbene complex was obtained.[4d] Several other related examples are also known.[14] Consequently, it is not unlikely that either fluorenylidene (15) or its molybdenum–carbene complex might be the intermediate which dimerizes to give 14 or abstracts hydrogen from the solvent to give 13. The two carbon sulfur bonds may be cleaved stepwisely. Alternatively, the sulfur-stabilized radical formed in the first step may abstract hydrogen from THF to give a thioether which may further react with the molybdenum species to reduce this second carbon–sulfur bond.

12 15

Attempts to desulfurize adamantanone thioketal 12 under these conditions were unsuccessful and only starting material was recovered.

In summary, we have depicted that benzylic-, aryl-, or α-acyl-activated carbon–sulfur bonds can be readily reduced by the treatment with $Mo(CO)_6$ in THF. The reaction may proceed via a radical-like mechanism.

Experimental Section

An NMR spectra were recorded on JEOL 60-HL and Bruker WM 250 spectrometers using tetramethylsilane (Me_4Si) as the internal standard, infrared spectra on a Perkin-Elmer 283 spectrophotometer, and mass spectra on a VG 7070F mass spectrometer. Melting points are uncorrected. All mercaptans were prepared according to the standard procedures.[15]

General Procedure for the Desulfurization Reaction. A THF solution (ca. 40 mL) of sulfur-containing compounds (2 mmol) and 1–2 equiv of $Mo(CO)_6$ was heated under reflux for 12–16 h. After cooling, the mixture was filtered, and the filter cake was washed with ether. The filtrate was evaporated in vacuo, and the residue was chromatographed on silica gel and eluted with petroleum ether (60–80 °C) to give the desired product.

Desulfurization of 1-Naphthalenemethanethiol (1). According to the general procedure, the reaction of 1 (0.348 g, 2 mmol) and $Mo(CO)_6$ (0.528 g, 2 mmol) in THF (ca. 40 mL) afforded 1-methylnaphthalene (0.224 g, 79%), which exhibits identical spectroscopic properties with those of the authentic sample.

Desulfurization of 2-Naphthalenemethanethiol (2). Following the general procedure, a mixture of 2 (0.174 g, 1 mmol) and $Mo(CO)_6$ (0.264 g, 1 mmol) were transformed into 2-

(12) Nelson, S. J.; Detre, G.; Tanabe, M. *Tetrahedron Lett.* **1973**, 447.
(13) Zervas, L.; Photake, I. *J. Am. Chem. Soc.* **1962**, *84*, 3887.

(14) (a) Petz, W. *J. Organomet. Chem.* **1979**, *172*, 415. (b) Dettlaf, G.; Hubener, P.; Klimes, J.; Weiss, E. *J. Organomet. Chem.* **1982**, *229*, 63. (c) Daub, J.; Erhardt, U.; Kappler, J.; Trautz, V. *J. Organomet. Chem.* **1974**, *69*, 423. (d) Daub, J.; Kappler, J. *J. Organomet. Chem.* **1974**, *80*, C5.

(15) (a) Urquhart, G. G.; Gates, J. W., Jr.; Connor, R. *Org. Synth.* **1941**, *21*, 36. (b) Vogel, A. I. "A Textbook of Practical Organic Chemistry", 4th ed.; Longman: London, 1978; p 583.

methylnaphthalene (0.095 g, 67%), which is identical in every aspect with the authentic sample.

Desulfurization of 4-Methoxybenzyl Mercaptan (3). According to the general procedure, **3** (0.308 g, 2 mmol) and $Mo(CO)_6$ (0.528 g, 2 mmol) in THF (ca. 40 mL) were converted to 4-methylanisol (0.17 g, 71%), which shows identical physical properties with those of the authentic sample.

Desulfurization of 4-Carboxybenzyl Mercaptan (4). According to a similar procedure, a mixture of **4** (0.157 g, 0.937 mmol) and $Mo(CO)_6$ (0.247 g, 0.937 mmol) in THF (ca. 40 mL) was transformed to 4-toluic acid (0.078 g, 67%), which exhibits the same physical properties as those of the authentic sample.

Desulfurization of 4-Bromobenzyl Mercaptan (5). A THF solution of **5** (0.203 g, 1 mmol) and $Mo(CO)_6$ (0.264 g, 1 mmol) was converted to 4-bromotoluene (0.108 g, 63%), which was characterized by comparing spectroscopic properties with those of the standard sample.

Desulfurization of 4-Chlorobenzyl Mercaptan (6). By a method similar to that described above, **6** (0.333 g, 2 mmol) was reduced to give 4-chlorotoluene (0.163 g, 61%), which exhibits identical spectroscopic properties with those of the authentic sample.

Desulfurization of α-(Thiomethoxy)acetophenone (7). Compound **7** (0.166 g, 1 mmol) and $Mo(CO)_6$ (0.264 g, 1 mmol) in THF (ca. 40 mL) were converted in a similar manner as described in the general procedure into the reduced product, acetophenone (0.068 g, 57%), which is identical in every aspect with the authentic compound.

Desulfurization of 2-Thionaphthol (8). The mercaptan **8** (0.322 g, 2.01 mmol) and $Mo(CO)_6$ (0.528 g, 2 mmol) in THF (ca. 40 mL) were transformed according to the procedure described above to yield naphthalene (0.112 g, 43%), which is identical with the authentic compound.

Desulfurization of 9-Fluorenone Thioketal 9. A mixture of **9** (0.256 g, 1 mmol) and $Mo(CO)_6$ (0.264 g, 1 mmol) in THF (ca. 30 mL) was refluxed for 12 h to give a brown-colored suspension. After filtration, the filter cake was washed with diethyl ether several times. The combined ether solution was evaporated, and the residue was chromatographed on silica gel and eluted with petroleum ether. From the first fraction (ca. 100 mL), **13** (0.069 g, 42%) was obtained, which exhibits the same properties as those of the authentic sample. The second fraction was identified as **14** (0.055 g, 34%): mp 190–191.5 °C (lit.[16] mp 187 °C); mass spectrom, *m/e* 328, 164; ^1H NMR ($CDCl_3$) δ 7.03 (8 H, m), 7.48, (4 H, m), 8.13 (4 H, m).

Desulfurization of 1-Adamantyl 2-Naphthylmethyl Sulfide (10). Compound **10** (0.616 g, 2 mmol) was allowed to react with $Mo(CO)_6$ (1.056 g, 4 mmol) in THF (ca. 40 mL) at refluxing temperature for 16 h. After cooling the mixture was filtered, and the filter cake was washed with ether. The organic solution was evaporated in vacuo to give the brownish residue, which was chromatographed on silica gel and eluted with petroleum ether. The first fraction afforded 2-methylnaphthalene (0.1 g, 73% based on unrecovered starting material), which exhibits the same spectroscopic data as those of the authentic sample. Further elution with petroleum ether yielded 1-adamantanethiol (0.085 g, 49% based on unrecovered starting material), which shows identical properties with those of the authentic material, and recovered the starting material (0.3 g, 49%).

Registry No. **1**, 5254-86-4; **2**, 1076-67-1; **3**, 6258-60-2; **4**, 39088-65-8; **5**, 19552-10-4; **6**, 6258-66-8; **7**, 5398-93-6; **8**, 91-60-1; **9**, 7049-31-2; **10**, 99282-02-7; **11**, 34301-54-7; **13**, 86-73-7; **14**, 746-47-4; 1-methylnaphthalene, 90-12-0; 2-methylnaphthalene, 91-57-6; 4-methylanisole, 104-93-8; 4-toluic acid, 99-94-5; 4-bromotoluene, 106-38-7; 4-chlorotoluene, 106-43-4; acetophenone, 98-86-2; naphthalene, 91-20-3.

(16) Campaigne, E.; Reid, W. B., Jr. *J. Am. Chem. Soc.* **1946**, *46*, 769.

(17) In this paper the periodic group notation in accord with recent actions by IUPAC and ACS nomenclature committees has been included. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

Formation of a Neutral Covalent Adduct in the Nucleophilic Aromatic Substitution Reaction Involving a Carbon Leaving Group

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Our interest in the field of nucleophilic aromatic substitution reactions[1] has prompted us to investigate the mechanism of substitution of substrates bearing the scarcely studied carbon leaving groups. We have studied the reaction of MeO^- ion in MeOH with 4-(trichloromethyl)quinazoline (**1**), a substrate somewhat related to 2-methyl-4-(tribromomethyl)quinazoline, that has been shown to be probably involved[2] in the aromatic substitution reaction of a CBr_3 group.

The reaction of **1** with methoxide ion at room temperature yields chloroform and 4-methoxyquinazoline (**2**). Undoubtedly, as observed in the 1,3,5-triazine ring,[3] the CCl_3 group is easily replaced because compound **1** is activated by two aza groups and the annelated benzene ring. Indeed, the substitution of a trihalo group seems to be strongly affected by the presence of electron-withdrawing groups. Thus poorly activated substrates, such as (trichloromethyl)pyridine[4] and -benzothiazole[5] derivatives do not undergo the aromatic substitution reaction. Interestingly, however, 2-(trifluoromethyl)quinoline is the only substrate in a large group of trifluoromethyl-substituted heterocyclic compounds to undergo the aromatic substitution reaction rather than a side-chain reaction.[6]

From a preparative point of view, the replacement of the CCl_3 group of **1** with the methoxy group is similar to the replacement of other more common leaving groups. However, the UV and ^1H NMR spectral features of this reaction of **1** are different from those of the reactions that follow the usual aromatic substitution mechanism involving the steady-state formation of an intermediate σ adduct.

Upon addition of MeO^- ion (10^{-3} M) to a 10^{-4} M methanol solution of **1** the following changes are observed. At first (Figure 1) the absorbance of **1** (λ_{max} 315 nm) decreases, and a broad absorbance increase is observed in the 260–280-nm range (λ_{max} 268 nm, isosbestic point 293 nm). After some time (nearly 1 h at room temperature) this spectrum begins to evolve toward that of 4-methoxyquinazoline (λ_{max} 262, 296, and 308 nm). This further change is nearly 100 times slower than the former and is characterized by five isosbestic points, at 275, 294, 298, 306, and 310 nm, respectively (Figure 2).

The reaction has also been monitored by ^1H NMR spectroscopy. The ^1H NMR spectrum of **1** (Figure 3a) is gradually replaced by the spectrum reported in Figure 3b, showing the partial disappearance of **1** and the appearance of new signals upfield with respect to those of **1**. If at this point the temperature is decreased, a reversible change can be observed in the relative intensities of the signals of **1** and the new ones (Figure 3c), in agreement with the fact that this situation corresponds to an equilibrium between **1** and another species (or possibly with a mixture of rapidly

(1) Annulli, A.; Mencarelli, P.; Stegel, F. *J. Org. Chem.* **1984**, *49*, 4065.
(2) Siegle, J.; Christensen, B. E. *J. Am. Chem. Soc.* **1951**, *73*, 5777.
(3) Schaefer, F. C.; Ross, J. H. *J. Org. Chem.* **1964**, *29*, 1527.
(4) Kreutzberger, A. *J. Am. Chem. Soc.* **1957**, *79*, 2629.
(5) Holan, G.; Samuel, E. L. *J. Chem. Soc. C* **1967**, 25.
(6) Kobayashi, Y.; Kumadaki, I. *Acc. Chem. Res.* **1978**, *11*, 197.

0022-3263/85/1950-5415$01.50/0