pair-aryl interaction in an unstrained example of $I^{+\cdot}$.

Both 6-Me and 7-Me fall only slightly above the correlation line (2.3 and 0.9 kcal/mol, respectively), but the interplay between effects on the neutral and cationic forms is of course not clear. The effect of 3,6-dimethyl substitution on ground-state conformation is substantial, but changes in $E^{\circ\prime}$ deviation from the correlation line are small. 4A-Me is only 0.6 kcal/mol more difficult to oxidize in solution than is 4-Me when adjustments for HOMO energy are made by using the correlation line. In contrast, 4,5-dimethyl substitution should not affect the conformation significantly, but the 4B-Me deviation is -1.3 kcal/mol from the value for 4-Me. Methylating the benzene ring causes a larger increment in $E^{\circ\prime}$ than is accounted for in employing the correlation line. This would occur if solvation energy differences were significant and is consistent with data on para-substituted dimethylanilines, which show a slope greater than 1 in an $E^{\circ\prime}$ vs. IP_1 plot.[18]

Our data make it clear that quantitative interpretation of $E^{\circ\prime}$ differences is full of pitfalls for the unwary.

Experimental Section

Compound preparations are mainly described in the earlier paper.[1]

1,3,5,6-Tetramethyl-2,2-tetramethylenebenzimidazole [(12B-Me). A mixture of 1.0 g (6.1 mmol) of 4,5-dimethyl-*N*,*N*′-dimethyl-*o*-phenylenediamine, 5.1 g (61 mmol) of cyclopentanone, and 10 mL of toluene was refluxed on a water separator for 6 h, concentrated, and Kugelrohr distilled (0.02 torr, 150 °C), giving 1.08 g (80%) of a yellow oil: ^{1}H NMR δ 5.80 (s, 2 H), 2.61 (s, 6 H), 2.06 (s, 6 H), 1.4-3.0 (m, 8 H); empirical formula determined by high-resolution mass spectroscopy.

Photoelectron spectroscopy measurements were made on a Varian 1EE-15 instrument, and the data were handled as previously described.[3] A picture of each photoelectron spectrum appears in the thesis of L.A.G.[19] Calculations were performed on a Harris/7 computer.

Acknowledgment. We thank the National Science Foundation for partial financial support of this work, both through research grants and the Major Instrument Program.

Registry No. 4-H, 95-54-5; 4-Me, 704-01-8; 4A-Me, 66102-30-5; 4B-H, 3171-45-7; 4B-Me, 54929-05-4; 5-Me, 3204-31-7; 6-H, 3476-89-9; 6-Me, 2427-06-7; 6A-H, 66102-39-4; 6A-Me, 66102-31-6; 6B-H, 10579-68-7; 6B-Me, 66102-32-7; 7-H, 6516-89-8; 7-Me, 19560-66-8; 8-H, 39161-58-5; 8-Me, 39161-60-9; 9-Me, 66102-33-8; 12-Me, 66102-34-9; 12B-Me, 75751-20-1; 14, 7140-45-6; 14A, 66102-38-3; 14B, 66102-37-2; 15, 73023-02-6; 4,5-dimethyl-*N*,*N*′-dimethyl-*o*-phenylenediamine, 75751-21-2; cyclopentanone, 120-92-3.

(19) Grezzo, L. A. Thesis, University of Wisconsin-Madison, 1980.

Hydrozirconation of Thioketones. A Simple, Convenient Entry into a Variety of Organosulfur Compounds. An Interesting Ether Synthesis

David E. Laycock and Howard Alper*[1]

Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 9B4

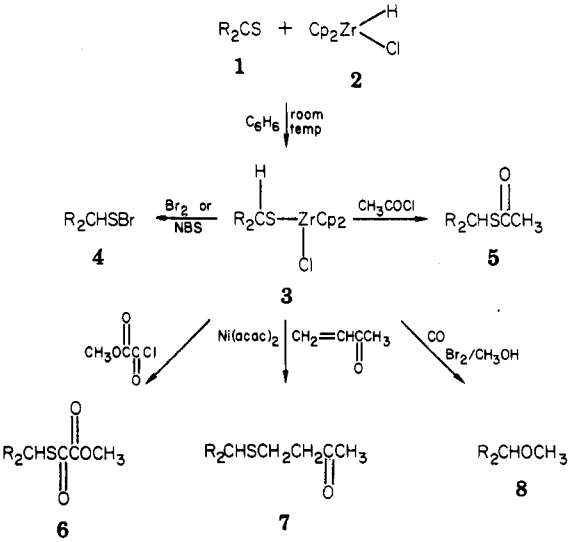
Received June 6, 1980

Aromatic and aliphatic thioketones undergo hydrozirconation at room temperature with $(C_5H_5)_2Zr(H)Cl$ to give sulfur–zirconium compounds, $R_2CHSZr(Cl)(C_5H_5)_2$. Cleavage of the latter by bromine or *N*-bromosuccinimide affords sulfenyl bromides, acid chlorides give thioesters, methyloxalyl chloride gives a thiooxalate, methyl vinyl ketone [catalyzed by Ni(II)] results in the formation of the β-keto sulfide, and carbonylation followed by bromination in alcohol affords the ether. Very mild conditions are utilized for all of these reactions. Mechanisms are proposed for the interesting ether synthesis.

The past 10 years have witnessed an increased awareness of the importance of transition-metal organometallic compounds as reagents for organic synthesis.[2] Of the many such reagents developed during this period, hydridochlorobis(cyclopentadienyl)zirconium is one of the most important. Excellent work by Schwartz and co-workers[3] has demonstrated that facile hydrozirconation of olefins affords organozirconium species which can undergo subsequent cleavage by various reagents (peroxide, halogen, etc.) to give useful organic products.

We have, for some time, been examining the chemistry of thioketones in terms of applications to organic synthesis[4] and to the preparation of novel organometallic complexes.[5] It seemed conceivable that thioketones should, like olefins, experience hydrozirconation and that sulfur–zirconium bond cleavage of the generated zirconium intermediate may constitute an entry into a variety of interesting or-

Scheme I



(1) E. W. R. Steacie Fellow, 1980–1982.
(2) H. Alper, Ed., "Transition Metal Organometallics in Organic Synthesis", Vol. I, Academic Press, New York, 1976; Vol. II, 1978.
(3) J. Schwartz, *J. Organomet. Chem. Libr.*, 1, 461 (1976); J. Schwartz and J. A. Labinger, *Angew. Chem., Int. Ed. Engl.*, 15, 333 (1976), and references cited therein.
(4) H. Alper and W. G. Root, *J. Am. Chem. Soc.*, 97, 4251 (1975).
(5) H. Alper, N. D. Silavwe, G. I. Birnbaum, and F. R. Ahmed, *J. Am. Chem. Soc.*, 101, 6582 (1979).

0022-3263/81/1946-0289$01.00/0

Table I. Hydrozirconation Reaction Products

thioketone	cleavage reagent	product[a]	yield, %	IR (ν_{CO}) cm^{-1}	^1H NMR,[b] δ	^{13}C NMR,[b,c] δ	mass spectrum, *m/e*
$(p\text{-}CH_3OC_6H_4)_2CS$	Br_2	$(p\text{-}CH_3OC_6H_4)_2CHSBr$	40		3.78 (s, 6 H, OCH_3), 5.28 (s, 1 H, CH), 6.80 (d, 4 H, aromatic, J = 9 Hz), 7.25 (d, 4 H, aromatic)	55.22 (OCH_3), 78.96 (CHS), 113.75, 128.49, 134.87, 158.90 (aromatic)	
	CH_3COCl	$(p\text{-}CH_3OC_6H_4)_2CH\text{-}SC(O)CH_3$	80	1690	2.24 (s, 3 H, $COCH_3$), 3.72 (s, 6 H, OCH_3), 5.73 (s, 1 H, CH), 6.78 (d, 4 H, aromatic, J = 9 Hz), 7.21 (d, 4 H, aromatic)		302 (M^+), 259 [$(M - COCH_3)^+$]
	$ClC(O)C(O)OCH_3$	$(p\text{-}CH_3OC_6H_4)_2CHSC(O)C(O)OCH_3$	62	1765, 1690	3.76 (s, 6 H, OCH_3), 3.86 (s, 3 H, $COOCH_3$), 5.90 (s, 1 H, CH), 6.80 (d, 4 H, aromatic, J = 9 Hz), 7.28 (d, 4 H, aromatic)		
	$CH_2{=}CHC(O)CH_3$	$(p\text{-}CH_3OC_6H_4)_2CHSCH_2CH_2C(O)CH_3$	84	1720	2.10 (s, 3 H, $COCH_3$), 2.62 (s, 4 H, SCH_2CH_2),[d] 3.80 (s, 6 H, OCH_3), 5.12 (s, 1 H, CHS), 6.80 (d, 4 H, aromatic, J = 9 Hz), 7.38 (d, 4 H, aromatic)	26.13 ($COCH_3$), 29.96 (CH_2CO), 43.20 (SCH_2), 53.32 (CHS), 55.26 (OCH_3), 113.91, 129.26, 133.54, 158.64 (aromatic), 166.79 ($COCH_3$)	
	CO, Br_2/CH_3OH	$(p\text{-}CH_3OC_6H_4)_2CHOCH_3$	82		3.40 (s, 3 H, $CHOCH_3$), 3.70 (s, 6 H, OCH_3), 5.12 (s, 1 H, CHO), 6.78 (d, 4 H, aromatic, J = 9 Hz), 7.19 (d, 4 H, aromatic)		258 (M^+)
	CO, Br_2/C_2H_5OH	$(p\text{-}CH_3OC_6H_4)_2CHOC_2H_5$	55		1.13 (t, 3 H, CH_3CH_2), 3.50 (q, 2 H, CH_3CH_2), 3.78 (s, 6 H, OCH_3), 5.31 (s, 1 H, CH), 6.88 (d, 4 H, J = 8 Hz, aromatic), 7.30 (d, 4 H, aromatic)		272 (M^+)
$(p\text{-}CH_3C_6H_4)_2CS$	NBS	$(p\text{-}CH_3C_6H_4)_2CHSBr$	50		2.30 (s, 6 H, CH_3), 4.92 (s, 1 H, CH), 7.08 (m, 8 H, aromatic)		
	CH_3COCl	$(p\text{-}CH_3C_6H_4)_2CHSCOCH_3$	66	1698	2.30 (s, 9 H, methyls), 5.86 (s, 1 H, CH), 7.15 (m, 8 H, aromatic)	21.04 (methyls on benzene rings), 30.29 ($COCH_3$), 51.38 (CHS), 193.81 (CO)	270 (M^+), 227 [$(M - COCH_3)^+$]
	CO, Br_2/CH_3OH	$(p\text{-}CH_3C_6H_4)_2CHOCH_3$	65		2.28 (s, 6 H, CH_3), 3.35 (s, 3 H, OCH_3), 5.18 (s, 1 H, CHO), 7.15 (m, 8 H, aromatic)	21.10 (methyls on benzene rings), 56.89 (OCH_3), 85.12 (CHO)	226 (M^+)

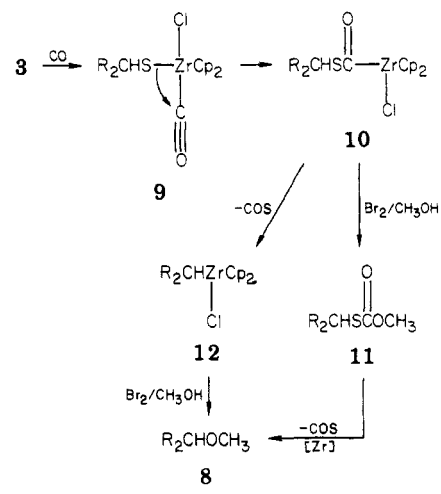
$[p\text{-}(CH_3)_2NC_6H_4]_2CS$	CH_3COCl	$[p\text{-}(CH_3)_2NC_6H_4]_2CHSCOCH_3$	82	1695	2.34 (s, 3 H, $COCH_3$), 2.85 (s, 12 H, dimethylamino protons), 5.76 (s, 1 H, CHS), 6.58 (d, 4 H, aromatic, J = 9 Hz), 7.14 (d, 4 H, aromatic)	328 (M^+), 285 [$(M - COCH_3)^+$]
$p\text{-}CH_3OC_6H_4CSPh$	CH_3COCl	$p\text{-}CH_3OC_6H_4C(Ph)HSCOCH_3$	60	1695	2.32 (s, 3 H, $COCH_3$), 3.75 (s, 3 H, OCH_3), 5.88 (s, 1 H, CHS), 6.6–7.4 (m, 9 H, aromatic)	272 (M^+)
	CO, Br_2/CH_3OH	$p\text{-}CH_3OC_6H_4C(Ph)HOCH_3$	95		3.30 (s, 3 H, $CHOCH_3$), 3.70 (s, 3 H, OCH_3), 5.16 (s, 1 H, CHO), 6.6–7.4 (m, 9 H, aromatic)	228 (M^+)
thiocamphor	CH_3COCl	$C_{10}H_{17}SCOCH_3$	40	1695	0.8–2.5 (m, $C_{10}H_{17}$ unit, and s for $COCH_3$ at 2.33)	212 (M^+)
adamantanethione	CH_3COCl	(2-Ada)$SCOCH_3$[e]	66	1690		210 (M^+), 167 [$(M - COCH_3)^+$]
13	$ClC(O)C(O)OCH_3$	14	45	1765 (br), 1742, 1700, 1680	0.82, 0.90, 1.10, 1.13 (s each, 12 H, angular methyls of both epimers), 0.9–2.2 (m, 30 H, protons of rings B, C, and D of both isomers), 3.90, 3.92 (s, 6 H, CH_3OCO of α and β isomers), 4.80 (m, 1 H, CHS of β), 4.98 (m, 1 H, CHS of α), 5.38, 5.68, 6.00 (m, 6 H, olefinic protons of the two isomers)	388 (M^+)
	CH_3COCl	15, R = CH_3	60	1735, 1690	0.85, 1.08 (s, 6 H, angular methyls), 2.28 (s, 3 H, CH_3COS), 0.8–2.5 (m, 15, protons of B, C, and D rings), 4.75 (m, 1 H, CHS), 5.30, 5.62 (m, 3 H, unsaturated protons)	344 (M^+)
	$CH_3CH{=}CHCOCl$	15, R = $CH_3CH{=}CH$	76	1740	0.92, 1.14 (s, 6 H, angular methyls), 1.95 (dd, 3 H, $CH_3CH{=}CH$), 0.9–2.6 (m, 15 H, protons of B, C, and D rings), 4.80 (m, 1 H, CHS), 5.37–5.90 (m, 3 H, unsaturated protons of ring A), 6.05 (m, 1 H, $CH_3CH{=}CHCO$), 6.95 (m, 1 H, $CH_3CH{=}CHCO$)	

Table I (*Continued*)

thioketone	cleavage reagent		product[a]	yield, %	IR (ν_{CO}) cm^{-1}	^1H NMR,[b] δ	^{13}C NMR,[b,c] δ	mass spectrum, *m/e*
	CH_2=CHCOCH$_3$	16		65	1740, 1715	0.85, 1.15 (s, 6 H, angular methyls), 0.95–3.0 (m, 15 H, protons of rings B, C, and D), 2.20 (s, 3 H, $COCH_3$), 2.65 (s, 4 H, SCH_2CH_2), 3.92 (m, 1 H, CHS), 5.32–6.00 (m, 3 H, unsaturated protons)		

[a] Satisfactory analytical data were obtained for all new compounds. [b] $CDCl_3$ with tetramethylsilane as the internal standard. [c] Assignments were made by recording spectra in the fully decoupled and partially decoupled modes. [d] In benzene-d_6, the two methylene groups appeared as triplets at δ 2.15 and 2.56. [e] 2-Ada = 2-adamantyl.

Scheme II



ganosulfur compounds.[6,7] The results described below indeed bear out these expectations and illustrate other interesting aspects as well.

The hydrozirconation of aromatic and aliphatic thiones (**1**) by hydridochlorobis(cyclopentadienyl)zirconium (**2**) in benzene at room temperature is complete in less than 1 h (Scheme I). The reaction is simple to monitor, since the generated sulfur–zirconium compound (**3**) is usually yellow, while the reactant thiones are blue, purple, or orange.

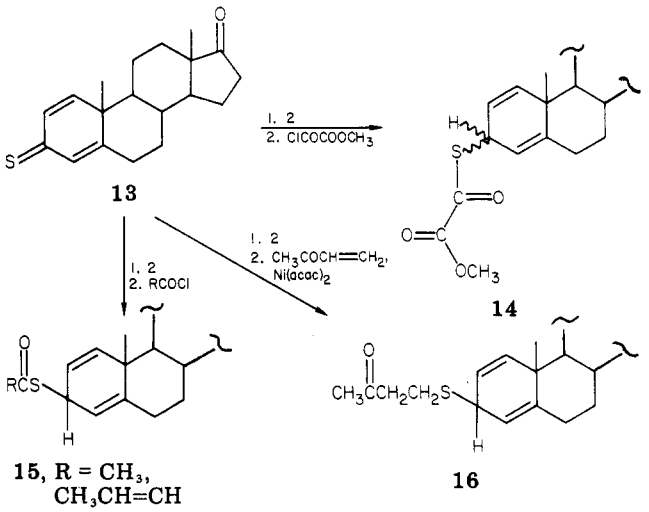
Bromination of **3** with bromine or *N*-bromosuccinimide (NBS) results in the formation of the sulfenyl bromide **4**. Treatment of the sulfur–zirconium intermediate **3** with an acid chloride such as acetyl chloride affords the thioesters **5** in fine yields, while the thiooxalate **6** was obtained by the use of methyloxalyl chloride as the substrate. Nickel(II)-catalyzed conjugate addition of **3** to methyl vinyl ketone in tetrahydrofuran affords the β-keto sulfide **7**. Excellent yields of ethers **8** were realized by carbonylation of **3** at room temperature and atmospheric pressure, followed by treatment with bromine in methanol (ethanol was also used). The structures of the reaction products, **4**–**8**, were elucidated on the basis of analytical and spectral data and, in some cases, by comparison with authentic materials. Product yields and pertinent spectral data are given in Table I.

Compounds **4**–**6** arise by electrophilic cleavage of the sulfur–zirconium bond of **3**. The formation of ethers **8**, by the room-temperature carbonylation of **3**, can be accounted for by initial binding of carbon monoxide to the metal (**9**), followed by ligand migration (**10**, Scheme II). Cleavage of the latter by bromine in methanol would give the thiocarbonate **11**, the expected reaction product. The zirconium byproduct may then induce elimination of carbon oxysulfide from **11**. The elimination of carbon dioxide from carbonates has been reported to occur at high temperatures.[8,9]

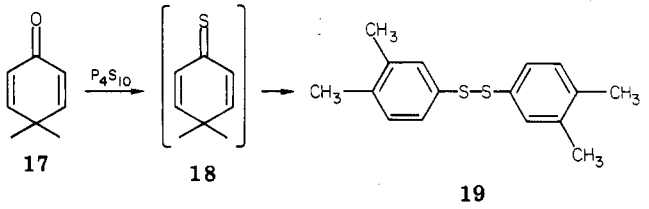
As an alternative mechanism, loss of carbon oxysulfide may occur from **10** to give **12**. Exposure of the latter to bromine in methanol would afford the ether. However, the failure to isolate any methyl ether from the reaction of $PhCH_2CH_2ZrCp_2Cl$ (a compound related to **12**) with

(6) E. Block, "Reactions of Organosulfur Compounds", Academic Press, New York, 1978.
(7) L. Field, *Synthesis*, 713 (1978).
(8) J. M. Prokipcak and T. H. Breckles, *Can. J. Chem.*, **49**, 914 (1971).
(9) E. Muller, H. Witt, and H. Holtschmidt, *Angew. Chem.*, **82**, 79 (1970).

Scheme III



Scheme IV



bromine in methanol is evidence against this alternate pathway.

Finally, it was of interest to examine the hydrozirconation and ensuing electrophilic cleavage of an α,β-unsaturated thione, where 1,2- and 1,4-addition of the zirconium reagent may occur. The diene thione, 3-thioxoandrosta-1,4-dien-17-one (**13**), was chosen for this study. Selective 1,2-addition occurred in all of the examined reactions. For example, hydrozirconation of **13** (Scheme III) followed by reaction with methyloxalyl chloride afforded **14** as a 2:1 mixture of 3β to 3α epimers (determined by NMR spectroscopy, the axial proton at the 3-position of the β isomer occurring at higher field than the equatorial proton in the β epimer). Cleavage of the zirconium intermediate by acetyl or crotonyl chloride afforded **15** (R = CH_3, CH_3CH=CH) while conjugate addition of methyl vinyl ketone resulted in the formation of **16**. Compounds **15** and **16** were obtained as 3β-substituted androsta-1,4-dien-17-ones.

It was also planned to investigate the hydrozirconation of the hitherto unknown monocyclic thione **18**. However, thionation of **17** by conventional routes only gave the aromatic disulfide **19** (Scheme IV).

In conclusion, the hydrozirconation–electrophilic cleavage and the hydrozirconation–conjugate addition of thioketones are simple, convenient, one-pot methods for the preparation of useful organic sulfur compounds under very gentle conditions. Irrespective of the mechanistic details, the hydrozirconation–carbonylation reaction of thiones to ethers is an intriguing reaction.

Experimental Section

General Data. Infrared spectra were obtained by using a Unicam SP1100 spectrometer equipped with a calibration standard. ^1H NMR spectra were recorded on a Varian T-60 or HA-100 spectrometer using tetramethylsilane as internal standard. Carbon magnetic resonance spectra were recorded in the fully and partially decoupled modes by using a Varian FT-80 spectrometer. Mass spectral analyses were determined on an AEI MS902 spectrometer. A Fisher-Johns apparatus was used for melting point determinations. Elemental analyses were performed by the Butterworth Microanalytical Consultancy, Ltd., by Guelph Chemical Laboratories, and by Canadian Microanalytical Service Limited.

Hydridochlorobis(cyclopentadienyl)zirconium was either purchased from Alfa Inorganics and used as received or synthesized from dichlorobis(cyclopentadienyl)zirconium (Aldrich Chemical Co.). 4,4′-Dimethoxythiobenzophenone was obtained commercially (Aldrich Chemical Co.), and literature procedures were used for preparing the following thioketones: 4,4′-dimethylthiobenzophenone,[10] 4-methoxythiobenzophenone,[11] thiobenzophenone,[10] 4,4′-bis(dimethylamino)thiobenzophenone,[10] thiocamphor,[12] adamantanethione,[13] 3-thioxoandrosta-1,4-dien-17-one.[14]

Solvents were dried and purified by standard methods. All reactions were effected under a dry nitrogen atmosphere.

Attempted Synthesis of 18. The procedure of Scheeren and co-workers[10] was applied to 4,4-dimethylcyclohexa-2,5-dienone[15] (i.e., P_4S_{10}, $NaHCO_3$, CH_3CN, 30 °C). After 2, 6, or 18 h, only the disulfide **19** was isolated in 20–46% yield: ^1H NMR ($CDCl_3$) δ 2.28, 2.31 (s, 12 H, CH_3), 7.1–7.4 (m, 6 H, aromatic protons). Characteristic aromatic stretching vibrations were observed in the infrared spectrum. Thionation of **17** by P_4S_{10} in benzene, without sodium bicarbonate, again afforded **19**.

General Procedure for Hydrozirconation–Electrophilic Cleavage of Thioketones. To a stirred dispersion of **2** (2 mmol) in benzene (20 mL) was added the thioketone **1** or **13** (1.6 mmol) in benzene (10 mL). The reaction mixture was stirred until the solution became yellow or yellow-orange (1 h or less). Cleavage of **3** was effected by the following methods: (a) NBS or Br_2, 1.1 equiv of either reagent added as a powder (NBS) or in benzene (Br_2); (b) CH_3COCl or $CH_3OCOCOCl$, 1.1 equiv added and the solution stirred overnight; (c) CH_2=$CHCOCH_3$ (the hydrozirconation was effected in tetrahydrofuran), a mixture of the ketone (1.1 equiv) and $Ni(acac)_2$ (50 mg) in THF (10 mL) was added, and the solution was stirred for 1 h; (d) CO,Br_2/ROH, carbon monoxide was bubbled into the solution for 5–6 h, followed by addition of 5 mL of a 5% Br_2/ROH solution. Workup in all instances was carried out by filtration of the reaction mixture, rotary evaporation of the filtrate, and chromatography of the resultant crude product on silica gel.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council for support of this work.

Registry No. **1** (R_2 = (p-$CH_3OC_6H_4$)$_2$), 958-80-5; **1** (R_2 = (p-$CH_3C_6H_4$)$_2$), 1141-08-8; **1** (R_2 = [p-$(CH_3)_2NC_6H_4$]$_2$), 1226-46-6; **1** (R_2 = Ph and p-$CH_3OC_6H_4$), 1141-07-7; **2**, 37342-97-5; **4** (R_2 = (p-$CH_3OC_6H_4$)$_2$), 74684-88-1; **4** (R_2 = (p-$CH_3C_6H_4$)$_2$), 74684-89-2; **5** (R_2 = (p-$CH_3OC_6H_4$)$_2$), 70136-62-8; **5** (R_2 = (p-$CH_3C_6H_4$)$_2$), 74709-71-0; **5** (R_2 = [p-$(CH_3)_2NC_6H_4$]$_2$), 74709-72-1; **5** (R_2 = Ph and p-$CH_3OC_6H_4$), 74684-90-5; **6** (R_2 = (p-$CH_3OC_6H_4$)$_2$), 74684-91-6; **7** (R_2 = (p-$CH_3OC_6H_4$)$_2$), 74684-92-7; **8** (R_2 = (p-$CH_3OC_6H_4$)$_2$), 2186-95-0; **8** (R_2 = (p-$CH_3C_6H_4$)$_2$), 18939-92-9; **8** (R_2 = Ph and p-$CH_3OC_6H_4$), 7364-21-8; **13**, 57334-04-0; **14** (epimer 1), 74684-93-8; **14** (epimer 2), 74684-94-9; **15** (R = CH_3), 74709-73-2; **15** (R = CH_3CH=CH), 74709-74-3; **16**, 74709-75-4; **17**, 1073-14-9; **19**, 64346-07-2; (p-$CH_3OC_6H_4$)$_2CHOC_2H_5$, 74684-95-0; $C_{10}H_{17}SCOCH_3$, 74684-96-1; (2-Ada)$SCOCH_3$, 74684-97-2; thiocamphor, 7519-74-6; adamantanethione, 23695-65-0.

(10) J. W. Scheeren, P. H. J. Ooms, and R. F. J. Nivard, *Synthesis*, 149 (1973).
(11) A. Schöenberg and E. Frese, *Chem. Ber.*, **101**, 701 (1968).
(12) M. M. Campbell, G. M. Anthony, and C. J. W. Brooks, *Org. Mass Spectrom.*, **5**, 297 (1971).
(13) J. W. Griedanus, *Can. J. Chem.*, **48**, 3593 (1970).
(14) D. H. R. Barton, L. S. L. Choi, R. H. Hesse, M. M. Pechet, and C. Wilshire, *J. Chem. Soc., Perkin Trans. 1*, 1166 (1979).
(15) H. Alper and J. T. Edward, *J. Organomet. Chem.*, **16**, 342 (1969).