NMR δ 0.89 (t, 3, CH_3), 1.29 (br, 14, CH_2), 1.33 (s, 3, CH_3), 1.40-2.58 (m, 6, CH_2). Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99. Found: C, 75.58; H, 10.85.

Dimethyl (3*R*)-3-methyladipate: bp 102-104 °C (2 mm); $[\alpha]_D^{28}$ +6.1° (*c* 2.22) (lit.[21a] $[\alpha]^{28}_D$ +3.49°).

Dimethyl 4-oxononanedioate: bp 118-119 °C (1.5 mm); IR (neat) 1733 (ester C=O), 1710 cm^{-1} (C=O); ^1H NMR δ 1.45-1.76 (m, 4, CH_2), 2.18-2.82 (m, 8, $COCH_2$), 3.63 (s, 6, OCH_3). Anal. Calcd for $C_{11}H_{18}O_5$: C, 57.38; H, 7.88. Found: C, 57.37; H, 7.95.

Methyl 4-oxotridecanoate: bp 132-133 °C (12 mm); IR (neat) 1739 (ester C=O), 1717 cm^{-1} (C=O); ^1H NMR δ 0.89 (t, 3, CH_3), 1.27 (br s, 14, CH_2), 2.00-2.70 (m, 6, $COCH_2$), 3.67 (s, 3, OCH_3). Anal. Calcd for $C_{14}H_{26}O_3$: C, 69.38; H, 10.81. Found: C, 69.30; H, 10.72.

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New Binuclear NMR Shift Reagents for Olefins and Aromatics

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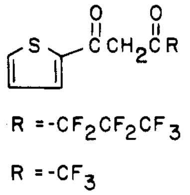
Binuclear complexes formed in solution from a lanthanide(III) β-diketonate and silver(I) β-diketonate have been studied as NMR shift reagents for olefinic and aromatic compounds. The shift reagent properties of a variety of silver β-diketonates with the praseodymium(III) or ytterbium(III) chelates of the ligands 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione, H(tta), and 4,4,5,5,6,6,6-heptafluoro-1-(2-thienyl)-1,3-hexanedione, H(hfth), have been evaluated and compared to binuclear shift reagents that have already been reported in the literature. The complexes of silver with the tta and hfth ligands, when employed with certain chiral lanthanide chelates, have resulted in better resolution of the resonances of *d* and *l* enantiomers than previously reported chiral binuclear complexes. The Ag(tta) and Ag(hfth) complexes are considerably more stable than the silver β-diketonates used in prior studies. Representative spectra of the resolution achieved for a mixture of *dl*-camphene are presented.

A wide range of oxygen- and nitrogen-containing compounds have been studied with lanthanide nuclear magnetic resonance shift reagents.[1-7] Recently, binuclear shift reagents suitable for use with olefins, aromatics, halogenated compounds, and phosphines have been reported.[8-13] The binuclear reagents are formed in solution from a lanthanide(III) β-diketonate and silver(I) β-diketonate. The active species is believed to be an ion pair between Ag(I) and a lanthanide tetrakis(chelate) anion;[9] however, other structures are possible for these binuclear complexes.[14] The silver in this complex bonds to the olefinic or aromatic substrate, and the NMR spectrum of the substrate exhibits shifts because of the lanthanide ion. We report a new set of binuclear complexes that involve silver compounds with the ligands 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione, H(tta), and 4,4,5,5,6,6,6-heptafluoro-1-(2-thienyl)-1,3-hexanedione, H(hfth). In certain



instances, binuclear complexes with one or more of these ligands produced better shifts in the NMR spectra of olefins or aromatics than the binuclear complexes already reported in the literature. In addition, these new silver β-diketonates appear to be more stable than the previously reported examples.[8-10]

Table I. Shifts in the Proton NMR Spectrum of Cyclohexene (0.1 M) in $CDCl_3$ with Various Yb(III) Shift Reagents (0.05 M)

shift reagent	olefin	α	β
$Yb(fod)_3/Ag(fod)$	5.41	3.13	2.41
$Yb(fod)_3/Ag(hfth)$	3.08	1.91	1.48
$Yb(fod)_3/Ag(tta)$	1.50	1.01	0.79
$Yb(hfth)_3/Ag(fod)$	1.74	1.18	0.94
$Yb(hfth)_3/Ag(tfa)$	0.75	0.61	0.51
$Yb(hfth)_3/Ag(hfth)$	1.67	1.12	0.90
$Yb(hfth)_3/Ag(tta)$	0.65	0.53	0.44
$Yb(tta)_3/Ag(fod$	0.02	0.23	0.22
$Yb(tta)_3/Ag(tfa)$	−0.25	0.06	0.12
$Yb(tta)_3/Ag(hfth)$	−0.21	0.09	0.14
$Yb(tta)_3/Ag(tta)$	−0.18	0.06	0.09

Results and Discussion

The nature of the interaction between the silver and the lanthanide in these binuclear complexes remains unknown.

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Table II. Shifts in the Proton NMR Spectrum of Toluene (0.1 M) in $CDCl_3$ with Various Pr(III) Shift Reagents (0.05 M)

shift reagent	*p*-H	*m*-H	*o*-H	Me
$Pr(fod)_3/Ag(tfa)$	−0.73	−0.59	−0.59	−0.35
$Pf(fod)_3/Ag(hfth)$	−0.77	−0.60	−0.60	−0.33
$Pf(fod)_3/Ag(tta)$	−0.75	−0.57	−0.57	−0.32
$Pr(hfth)_3/Ag(fod)$	−0.72	−0.53	−0.53	−0.28
$Pr(hfth)_3/Ag(tfa)$	−0.44	−0.44	−0.44	−0.21
$Pr(hfth)_3/Ag(hfth)$	−0.44	−0.44	−0.44	−0.23
$Pr(hfth)_3/Ag(tta)$	−0.80	−0.56	−0.56	−0.28
$Pr(tta)_3/Ag(fod)$	*a*			
$Pr(tta)_3/Ag(tfa)$	−0.42	−0.42	−0.42	−0.24
$Pr(tta)_3/Ag(hfth)$	*a*			
$Pr(tta)_3/Ag(tta)$	*a*			

[a] Not soluble at 0.05 M.

The silver might bridge to the lanthanide chelate through some type of coordination to the ligands or the interaction could be purely electrostatic.[10] Whatever the case, there is a larger distance between the lanthanide ion and the substrate in the binuclear complexes than there is for oxygen- or nitrogen-containing substrates bonded directly to the lanthanide ion. This larger distance in the binuclear complexes increases the concentration of shift reagent necessary to produce useful spectral clarifications. Achiral binuclear complexes with the tta and hfth ligands were evaluated as NMR shift reagents because of the possibility that the silver might perferentially bond to the sulfur atom of the ligand and reduce the distance between the lanthanide ion and the substrate.[15]

As a method of screening the various combinations of lanthanide chelates and silver β-diketonates, the shifts in the NMR spectrum of a solution of toluene (0.1 M) or cyclohexene (0.1 M) were recorded after addition of the binuclear complex (0.05 M). In previous studies, the two lanthanides of choice for the binuclear complexes were reported to be praseodymium(III) for upfield shifts and ytterbium(III) for downfield shifts.[9] Of the achiral complexes in those earlier reports, the binuclear complexes of $Pr(fod)_3$ with Ag(tfa), and $Yb(fod)_3$ with Ag(fod), were always found to result in the best shifts. In our studies, we have compared the combinations of $Pr(fod)_3$ or $Yb(fod)_3$ with Ag(fod), Ag(tfa), Ag(hfth), and Ag(tta). In addition, $Pr(tta)_3$, $Pr(hfth)_3$, $Yb(tta)_3$, and $Yb(hfth)_3$ were prepared and studied with Ag(fod), Ag(tfa), Ag(hfth), and Ag(tta). The results for the Yb(III) complexes are summarized in Table I, and the Pr(III) complexes in Table II. For the Yb(III) shift reagents, there is no combination that comes close to duplicating the results obtained with $Yb(fod)_3$ and Ag(fod). For Pr(III), however, there are four other complexes containing the thienyl group in at least one ligand that produce shifts similar to those observed with $Pr(fod)_3$ and Ag(tfa). Neither one of the five, though, is significantly better than the others.

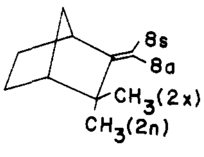
These results indicate that while the silver in the binuclear complexes with the tta and hfth ligands may bond to the sulfur atom of the thienyl group, any improvement in the distance term is offset by unfavorable changes to either the equilibrium constant for association or the angle term.[16] While the structure of these binuclear complexes is not known, it does appear that a rapid ligand exchange between the silver and the lanthanide occurs. Such an exchange is observed for lanthanide tris(chelates) in solution[1,17] and binuclear complexes with only one type of ligand.[9,14] For the mixed-ligand binuclear complexes employed in this study, it also appears that ligand exchange takes place. The shifts observed for 0.1 M cyclohexene with 0.05 M $Yb(hfth)_3$ and 0.05 M Ag(fod) (see Table I) were virtually identical with those observed when the shift reagent consisted of 0.033 M $Yb(hfth)_3$, 0.017 M $Yb(fod)_3$, and 0.05 M Ag(hfth). The same results were observed for two other pairs: 0.05 M $Yb(fod)_3$/0.05 M Ag(hfth) vs. 0.033 M $Yb(fod)_3$/0.017 M $Yb(hfth)_3$/0.05 M Ag(fod) and 0.05 M $Yb(fod)_3$/0.05 M Ag(tta) vs. 0.033 M $Yb(fod)_3$/0.017 M $Yb(tta)_3$/0.05 M Ag(fod). The similarity of the shifts for each pair indicates that for the mixed-ligand binuclear complexes a rapid ligand exchange occurs and, in each case, identical mixtures are produced.

In the selection of the best Pr(III) shift reagent from these pairs, a few things must be considered. The binuclear complexes with Ag(tta) and Ag(hfth) have resonances in the range of 6–7 ppm that may interfere with the aromatic signals of certain substrates and are more suited for the study of the aliphatic protons. In addition, the binuclear complexes with more than one type of ligand consist of undefined mixtures and are therefore not suitable for detailed structural analysis utilizing the McConnell–Robertson equation.[16]

One advantage of Ag(tta) and Ag(hfth) in comparison with Ag(tfa) is that they have a much longer shelf life. All of the silver β-diketonate complexes are light sensitive and are stored in light-proof containers. The Ag(tta), when first synthesized, is a pale yellow color, while Ag(tfa) and Ag(hfth) are white. Over the period of a few months, Ag(tfa) turns brown during storage and the smell of H(tfa) is apparent. In contrast, Ag(tta) and Ag(hfth) have retained their original color for 9 months now with no noticeable darkening. Silver(I) complexes can exhibit coordination numbers of 3 or 4, and the silver β-diketonates are probably oligomers in the solid state.[9,18] For the Ag(tta) and Ag(hfth) complexes, an oligomerization may result from the silver bonding to the sulfur atom of the thienyl group on neighboring ligands. Sulfur–silver(I) interactions are quite strong, and an added stability may result in comparison to those complexes without the thienyl groups.

In most applications involving achiral shift reagents, downfield shifts are preferred and Yb(III) is the lanthanide of choice. For the resolution of the NMR spectra of mixtures of enantiomers, however, Pr(III) shift reagents are often used.[19] Certain resonances of the *d* and *l* enantiomers of camphene, α-pinene, and limonene have been resolved into their *d* and *l* components in the presence of chiral binuclear complexes of Pr(III) and Yb(III) with Ag(I).[10,11] We have found that the chiral binuclear complexes formed in solution with $Pr(facam)_3$ or $Pr(hfbc)_3$ and Ag(hfth) result in better resolution of certain resonances of the *d* and *l* enantiomers of camphene than any of the previously reported chiral analogues containing Pr(III).

In Figure 1, a portion of the proton NMR spectrum of *dl*-camphene (0.1 M) after addition of $Pr(facam)_3$ (0.15 M) and Ag(hfth) (0.15 M) is shown. The 2x and 2n methyl resonances, initially singlets, are now split into two peaks



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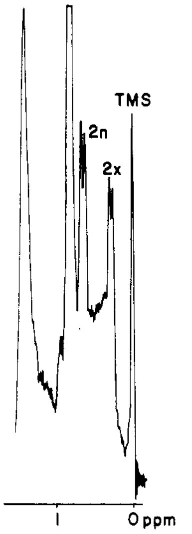

Figure 1. Proton NMR spectrum of 0.1 M *dl*-camphene in $CDCl_3$ with 0.15 M $Pr(facam)_3$ and 0.15 M Ag(hfth).

corresponding to the *d* and *l* enantiomers. The chiral shift reagents were tested over a range of concentrations relative to camphene. On our 60-MHz instrument, we were not able to resolve the 2x or 2n methyl resonances of camphene into their *d* and *l* components with either $Pr(facam)_3$ and Ag(tfa) or Ag(tta). It is interesting that a change of only one ligand of the binuclear complex can have such a pronounced effect on the resolution of the enantiomers. The reason for this is not known, but $Ag[Pr(facam)_3(hfth)]$ probably results in greater differences in the magnetic environment of the enantiomers of *dl*-camphene than the other chiral binuclear complexes. One further advantage of the combination of $Pr(facam)_3$ with Ag(hfth) is the complete solubility of this pair in $CDCl_3$ at concentrations up to 0.2 M. This is more convenient because the sample does not need to be filtered or spun in a centrifuge prior to taking the spectrum.

A comparison of the effects of the binuclear complexes consisting of $Pr(hfbc)_3$ with Ag(tfa), Ag(tta), and Ag(hfth) on *dl*-camphene is shown in Figure 2. In this case, the two olefin proton resonances, 8a and 8s, and the 2x methyl resonance, which are all singlets in the unshifted spectrum of *dl*-camphene, are resolved into their *d* and *l* components by each of the shift reagents. The results for the various reagents are quite similar, although inspection of the different spectra shows that with Ag(hfth), slightly larger shifts and better resolution of the *d* and *l* resonances are observed.

Figure 3 shows a comparison of the spectra of 0.1 M *dl*-camphene with 0.05 M $Yb(facam)_3$ and 0.05 M Ag(tfa), Ag(hfth), or Ag(tta). The resonances for the 2n methyl group are the easiest to compare in the shifted spectra. In the spectra with Ag(tta) and Ag(hfth), this peak is separated into *d* and *l* components, while it is not with Ag(tfa). In all cases, increasing the concentration of the shift reagent above 0.05 M led to better resolution of the 2n methyl resonance into the *d* and *l* components; however, the distinction provided by Ag(tta) was slightly better than that with Ag(hfth) and much better than that with Ag(tfa). At a concentration of 0.05 M shift reagent and 0.1 M camphene, these new shift reagents do not result in shifts or enantiomeric resolution comparable to that observed with the previously reported combination of $Yb(facam)_3$ and Ag(facam).[10] This combination has poor solubility though, typically precipitating out of solution at concentrations higher than 0.05 M. We have been able to add $Yb(facam)_3$ and Ag(tta) up to concentrations of 0.15 M with no solubility problems. At this concentration of $Yb(facam)_3$ and Ag(tta), the shifted spectrum for *dl*-camphene is almost identical with the best results produced by $Yb(facam)_3$ and Ag(facam). Ag(tta) also has a much longer shelf life than Ag(facam).

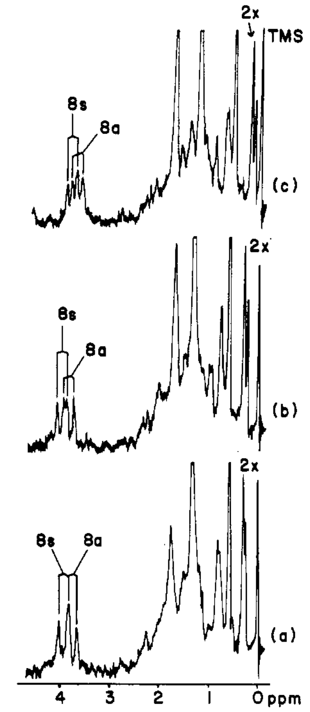

Figure 2. Proton NMR spectrum of 0.1 M *dl*-camphene in $CDCl_3$ with (a) 0.09 M $Pr(hfbc)_3$ and 0.09 M Ag(tfa), (b) 0.09 M $Pr(hfbc)_3$ and 0.09 M Ag(tta), and (c) 0.09 M $Pr(hfbc)_3$ and 0.09 M Ag(hfth).

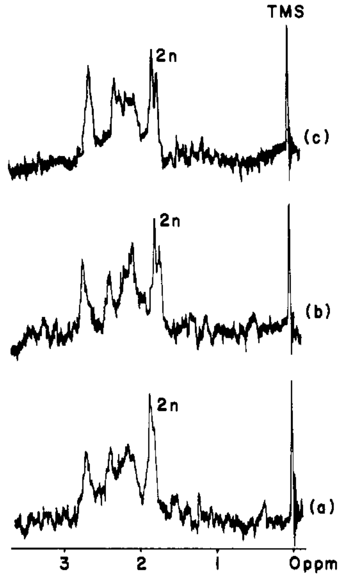

Figure 3. Proton NMR spectrum of 0.1 M *dl*-camphene in $CDCl_3$ with (a) 0.05 M $Yb(facam)_3$ and 0.05 M Ag(tfa), (b) 0.05 M $Yb(facam)_3$ and 0.05 M Ag(hfth), and (c) 0.05 M $Yb(facam)_3$ and 0.05 M Ag(tta).

Experimental Section

Apparatus. Proton NMR spectra were recorded with a Perkin-Elmer Model R24-A spectrometer at 60 MHz. Elemental analyses were performed by Robertson Lab., Florham Park, NJ.

Reagents. All chemicals were used as received without further purification. The 4,4,5,5,6,6,6-heptafluoro-1-(2-thienyl)-1,3-hexanedione, H(hfth), was obtained from Eastman Kodak Co., Rochester, NY. The 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione, H(fod), was obtained from PCR, Gainesville, FL. Camphene, chloroform-*d*, 1,1,1-trifluoro-2,4-pentanedione (H(tfa)), 3-(trifluoroacetyl)-*d*-camphor (H(facam)), 3-(heptafluorobutyryl)-*d*-camphor (H(hfbc)), and 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (H(tta)) were obtained from Aldrich Chemical Co., Milwaukee, WI.

Synthesis. The Ln(fod)$_3$, Ln(facam)$_3$, Ln(hfbc)$_3$, Ln(hfth)$_3$, and Ln(tta)$_3$ chelates were synthesized and purified according to the procedure reported by Springer et al.[20] for the preparation of Ln(fod)$_3$ complexes or purchased from Aldrich Chemical Co. The Ag(fod) and Ag(tfa) complexes were prepared by the literature method.[9]

(a) Preparation of [4,4,4-Trifluoro-1-(2-thienyl)-1,3-butanedionato]silver(I), Ag(tta). A solution of 2.8 g of H(tta) in 20 mL of methanol was neutralized with 3.2 mL of 4 M NaOH and was then added to a vigorously stirred solution of 2.2 g of $AgNO_3$ in 50 mL of distilled water. As the ligand was added, a pale yellow solid immediately formed. The solid was collected by suction filtration and dried in vacuo over P_4O_{10} overnight. The product was stored in a light-proof container; mp 147–149 °C. Attempted sublimation of Ag(tta) and the other silver β-diketonates used in this study led to decomposition. Anal. Calcd for $Ag(C_8H_4O_2F_3S)$: C, 29.20; H, 1.22. Calcd for $Ag(C_8H_4O_2F_3S)\cdot H_2O$: C, 27.68; H, 1.74. Found: C, 27.22; H, 1.35.

(b) Preparation of [4,4,5,5,6,6,6-heptafluoro-1-(2-thienyl)-1,3-hexanedionato]silver(I), Ag(hfth). This compound was prepared by an identical procedure to that described for Ag(tta). The white solid had a melting point of 168–170 °C. Anal. Calcd for $Ag(C_{10}H_4O_2F_7S)$: C, 27.99; H, 0.94. Found: C, 27.91; H, 1.21.

NMR Studies. In most cases, small amounts of an insoluble material remained after dissolving the binuclear complexes in chloroform-*d*, and the following procedure was used for obtaining the NMR spectra. The required amounts of the lanthanide chelate and the silver β-diketonate were placed in a test tube and a solution of the substrate and 1% Me_4Si in chloroform-*d* was added. The test tube was stoppered, shaken for 2 min, and centrifuged. The supernatant was removed by pipet and placed in an NMR tube for analysis. Since the silver compounds are somewhat light-sensitive, the test tube and NMR tube were covered with aluminum foil prior to recording the spectrum.

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Registry No. Yb(fod)$_3$, 18323-96-1; Yb(hfth)$_3$, 85565-58-8; Yb(tta)$_3$, 14644-89-4; Pr(fod)$_3$, 17978-77-7; Pr(hfth)$_3$, 85565-59-9; Pr(tta)$_3$, 14644-86-1; Pr(facam)$_3$, 38053-99-5; Pr(hfbc)$_3$, 38832-94-9; Yb(facam)$_3$, 38054-03-4; Ag(fod), 76121-99-8; Ag(hfth), 85565-60-2; Ag(tta), 16029-33-7; Ag(tfa), 69070-40-2; cyclohexene, 110-83-8; toluene, 108-88-3; *dl*-camphene, 565-00-4; *d*-camphene, 5794-03-6; *l*-camphene, 5794-04-7.

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Favorskii Rearrangements of α-Halogenated Acetylcycloalkanes. 4.[1-3] Stereochemistry of Cyclopropanonic Rearrangements and the Influence of Steric Factors on the Competing Formation of α-Hydroxy Ketones[†]

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It is shown that the marked stereoselectivity, in favor of 17α-methylated etio acid derivatives, of Favorskii rearrangements in protic and polar media of 17-brominated 20-keto steroids—somewhat diminished by a bulky 12α-substituent, such as an acetoxy group—is due, to an appreciable extent, to the influence of the 18-methyl group. Thus, the rearrangement of 17-bromo-3β-acetoxy-18-nor-5α-pregnan-20-one, which was synthesized from 3β-acetoxy-5α-androstan-17-one, proceeds with potassium bicarbonate in aqueous methanol much less stereoselectively than analogous rearrangements of 13-methylated 17-bromo 20-ketones, and in its reaction with potassium methoxide in absolute methanol the yield of the 17β-methyl 17α-etio ester even exceeds that of the 17α-methylated rearrangement product, in contradistinction to the results of equivalent reactions of 13-methylated substrates. It is also shown that in the absence of the 18-methyl group a 17β-hydroxy 20-ketonic substitution product and related adducts are obtained in high proportion, and it is concluded that the quasi-absence of such products in analogous reactions of 13-methylated 17-bromo 20-keto steroids is essentially due to the steric impediment exerted by this group to the formation of intermediate epoxy ethers. The results presented agree with the hypothesis of a competition between concerted and nonconcerted cyclopropanone formations from α-halo enolates, in part dependent on the polarity and protonicity of the medium, or possibly with that of gradients of mechanisms, and they support the intermediacy of epoxy ethers in the formation of α-hydroxy ketones as side products of Favorskii rearrangements.

We have suggested[1,8,9] that the complex stereochemistry of cyclopropanonic Favorskii rearrangements, in particular of α-halogenated acetylcycloalkanes such as α-halogenated 20-keto steroids, may be explained by the assumption of a competition between a concerted cyclopropanone formation favored in an aprotic and mildly polar medium and by a nonconcerted pathway involving the intermediacy of a dipolar species, favored in a protic and polar medium, and by the assumption that in certain cases the two pathways may be operative simultaneously.[10] In the case

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[†] Dedicated with admiration and gratitude to the memory of the late Dr. Hans Heusser (Feb 23, 1917–Oct 26, 1982), former Director, Hoffmann–La Roche & Co., Basle, Switzerland.

[1] Part 3: Engel, Ch. R.; Mērand, Y.; Côtē, J. *J. Org. Chem.* **1982**, *47*, 4485.

[2] This publication represents paper 51 in our series "Steroids and Related Products". Paper 50: Bończa-Tomaszewski, Z.; Engel, Ch. R. *Steroids* **1982**, *39*, 107.

[3] Reported in part at the 46th Congress of the French-Canadian Association for the Advancement of Sciences (ACFAS), Ottawa, May 1978, and in part in a paper presented to the 28th Congress of the International Union of Pure and Applied Chemistry, Vancouver, Aug 1981.

[4] Abbreviated from part of the D.Sc. thesis of P.L., Universitē Laval, Quebec, Quebec, Canada, 1967.