J_{AB} = 8.6, $J_{AA'}$ = 1.1, $J_{BB'}$ = 0.5 Hz, 4 H).

Phenyl Vinyl Sulfide Cycloaddition. This procedure was identical with that above except 0.270 g (1.0 mmol) of the furan and 0.136 g (1 mmol) of phenyl vinyl sulfide in 2 mL of toluene were used. Heating for 27 h gave the adduct, which was converted to 1,4-diphenylnaphthalene as above. Partial NMR (270 MHz, C_6D_6) of adduct: δ 2.15 (dd, J = 11.6, 3.4 Hz, 1 H), 2.86 (dd, J = 11.6, 9.4 Hz, 1 H), 4.22 (dd, J = 9.0, 3.1 Hz, 1 H).

***m*-(Trifluoromethyl)phenyl Vinyl Selenide Cycloaddition.** This procedure was identical with that above, except 0.270 g (1.0 mmol) of furan and 0.251 g (10 mmol) of **2a** in 2 mL of toluene were used. Heating at 100 °C for 18 h gave the adduct, which was converted to 1,4-diphenylnaphthalene as above. Partial NMR (270 MHz, C_6D_6) of adduct (major, minor): δ 2.21, 2.53 (dd, J = 11.8, 3.3 Hz; d, J = 7.1 Hz, 1 H), 2.89, 2.54 (dd, J = 9.6, 11.9 Hz; d, J = 4.6 Hz, 1 H), 4.07, 3.83 (dd, J = 9.4, 3.5 Hz; dd, J = 6.9, 4.9 Hz, 1 H).

Competitive Cycloaddition Rates. Sample Procedure. A solution of 0.027 g (0.1 mmol) of the furan, 0.018 g (0.1 mmol) of **1a**, and 0.014 g (0.1 mmol) of phenyl vinyl sulfide in 0.3 mL of C_6D_6 was sealed under N_2 into an NMR tube. The reaction mixture was heated to 90 °C for 2 h, and the relative amounts of starting materials and products were determined by NMR. The procedure was repeated for 12 h of heating as well. Data are summarized in Table 3 of the supplementary material.

Check of Reversibility. A solution of 0.041 g (0.15 mmol) of the furan and 0.018 g (0.1 mmol) of phenyl vinyl selenide in 0.3 mL of C_6D_6 with 0.5 drop of Et_3N was heated at 90 °C for 23 h, at which time the phenyl vinyl selenide had reacted. Then 0.037 g (0.15 mmol) of *m*-(trifluoromethyl)phenyl vinyl selenide was added. Heating an additional 24 h resulted in no liberation of phenyl vinyl selenide.

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Registry No. 1a, 35167-28-3; **1b**, 75599-83-6; **2a**, 77461-29-1; **2b**, 77461-30-4; **3a**, 77461-31-5; **3b**, 77461-32-6; **4a**, 77461-33-7; **4b**, 77461-34-8; **5a**, 72474-66-9; **5b**, 77461-35-9; (*E*)-**6a**, 60466-40-2; (*E*)-**6b**, 77461-36-0; (*E*)-**7a**, 68001-61-6; (*Z*)-**7a**, 68001-62-7; (*E*)-**7b**, 77461-37-1; (*Z*)-**7b**, 77461-38-2; (*E*)-**8a**, 60466-43-5; (*Z*)-**8a**, 60466-33-3; (*E*)-**8b**, 77461-39-3; (*Z*)-**8b**, 77461-40-6; (*E*)-**9a**, 67649-79-0; (*Z*)-**9a**, 68001-63-8; (*E*)-**9b**, 77461-41-7; (*Z*)-**9b**, 77461-42-8; **10a**, 77461-43-9; **10b**, 77461-44-0; **11a**, 77461-45-1; **11b**, 77461-46-2; **12a**, 56529-37-4; **12b**, 77461-47-3; **13a** (E = SMe), 77461-48-4; **13a** (E = TMS), 77461-49-5; **13a** (E = Me), 63017-57-2; **13a** (E = CO_2H), 77461-50-8; **13a** (E = Bu), 63831-76-5; **13a** (E = $C(OH)Et_2$), 77461-51-9; **13a** (E = $(CH_2)_3Ph$), 74866-73-2; **13a** (E = $C(CH_3)(OH)CH_2CH_2Ph$), 74866-72-1; **13a** (E = $C(OH)Me_2$), 77461-71-3; **13b** (E = PhSe), 77461-72-4; **13b** (E = TMS), 77461-73-5; **13b** (E = SMe), 77461-52-0; **13b** (E = CO_2H), 77461-53-1; **13b** (E = Bu), 74866-71-0; **13b** (E = Me), 77461-54-2; (*E*)-**14a**, 24225-10-3; (*Z*)-**14a**, 24213-07-8; (*E*)-**14b**, 77461-55-3; (*Z*)-**14b**, 77461-56-4; **15a**, 17417-82-2; **15b**, 77461-57-5; **17b**, 77461-58-6; (*E*)-**18b** (R^1 = Me), 77461-59-7; (*Z*)-**18b** (R^1 = Me), 77461-60-0; (*E*)-**18b** (R^1 = Bu), 77461-61-1; (*Z*)-**18b** (R^1 = Bu), 77461-62-2; (*E*)-**19b** (R^1 = Bu), 77461-63-3; (*Z*)-**19b** (R^1 = Bu), 77461-64-4; (*E*)-19b (R^1 = Me), 77481-98-2; (*Z*)-**19b** (R^1 = Me), 77461-65-5; **19b** (R^1 = H), 77461-66-6; **22a**, 38447-66-4; *endo*-**23**, 77461-67-7; *exo*-**23**, 77519-41-6; vinyl bromide, 593-60-2; benzeneselenenyl bromide, 34837-55-3; diphenyl diselenide, 1666-13-3; *m,m'*-bis(trifluoromethyl)diphenyl diselenide, 53973-75-4; 1-bromopropene, 590-14-7; bis[[*m*-(trifluoromethyl)phenyl]seleno]methane, 77481-99-3; dibromomethane, 74-95-3; bis(phenylseleno)methane, 20343-90-2; acetaldehyde, 75-07-0; acetone, 67-64-1; benzaldehyde, 100-52-7; isobutyraldehyde, 78-84-2; dimethyl disulfide, 624-92-0; *m,m'*-bis(trifluoromethyl)diphenyl disulfide, 18715-44-1; *m*-bromo-α,α,α-trifluorotoluene, 401-78-5; *m*-(trifluoromethyl)thiophenol, 937-00-8; *m*-(trifluoromethyl)phenyl vinyl sulfide, 75599-82-5; phenyl vinyl sulfide, 1822-73-7; diphenyl disulfide, 882-33-7; 2-(phenylthio)propene, 7594-43-6; 2-[[(*m*-trifluoromethyl)phenyl]thio]propene, 77461-68-8; phenyl methyl selenide, 4346-64-9; *m*-(trifluoromethyl)-phenyl methyl selenide, 37773-24-3; 1,3-diphenylisobenzofuran, 5471-63-6; 1,4-diphenylnaphthalene, 796-30-5; 1,2,3,4-tetrahydro-1,4-diphenyl-2-(phenylthio)-1,4-epoxynaphthalene, 77482-00-9; *endo*-1,2,3,4-tetrahydro-1,4-diphenyl-2-[[(*m*-trifluoromethyl)-phenyl]seleno]-1,4-epoxynaphthalene, 77461-69-9; *exo*-1,2,3,4-tetrahydro-1,4-diphenyl-2-[[(*m*-trifluoromethyl)phenyl]seleno]-1,4-epoxynaphthalene, 77519-42-7; propionaldehyde, 123-38-6; 3-pentanone, 96-22-0; 1-bromo-3-phenylpropane, 637-59-2; 4-phenyl-2-butanone, 2550-26-7; *m*-(trifluoromethyl)phenyl allyl selenide, 77461-70-2; phenyl allyl selenide, 14370-82-2; 3-(phenylthio)-1-butene, 701-75-7; crotyl chloride, 591-97-9; phenyl allyl sulfide, 5296-64-0.

Supplementary Material Available: Experimental details for the preparation of **2a, 4a, 4b, 5a, 6a, 8a, 8b, 9a, 10b, 11b, 13a** (E = *n*-Bu, $C(OH)Et_2$, $CH_2CH_2CH_2Ph$, $C(CH_3)(OH)CH_2CH_2Ph$), **13b** (E = *n*-Bu, CH_3), **15a, 15b, 17b, 18b** (R' = *n*-Bu), **19b** (R' = *n*-Bu), phenyl allyl selenide, *m*-(trifluoromethyl)phenyl allyl selenide, 3-(phenylthio)-1-butene. Kinetic data are summarized in tabular form for the relative acidities and rates of Diels–Alder addition (11 pages). Ordering information is given on any current masthead page.

Notes

Potential Causes of Erroneous Results of Analysis of Lanthanide-Induced Shifts: Contamination of $Ln(fod)_3$ NMR Shift Reagents with $Ln(fod)_3 \cdot Mfod$ and Self-Association of $Ln(fod)_3$

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Introduction

Lanthanide shift reagents have become valuable tools in NMR spectroscopy.[2] First of all these reagents have found widespread use in the simplification of NMR spectra of organic compounds able to act as lanthanide ligands. In addition, information on molecular structure in solution can be obtained by fitting the dipolar contribution to the bound shift of the complex between shift reagent and substrate to the McConnell–Robertson equation.[3] The evaluation of bound shifts requires knowledge of the equilibria involved in the complexation of the substrate (S) with the coordinatively unsaturated lanthanide shift reagent (L). For $Ln(fod)_3$ (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate) shift reagents several complexes should be envisaged, viz., LS, LS_2, and L_2.[4]

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0022-3263/81/1946-2784$01.25/0

Various procedures are used to obtain bound shifts or relative bound shifts for LS or LS_2 complexes from a series of NMR spectra of an organic substrate with different amounts of shift reagent.[4,5]

We now report two difficulties which were encountered in determining exact values for these shifts: impurities in shift reagents and self-association phenomena at high $Ln(fod)_3$ concentrations.

Results and Discussion

Usually, commercially available shift reagents are purified by drying and sublimation prior to use. During our investigations with the use of the lanthanide shift reagents $Ln(fod)_3$ we sometimes observed that commercial shift reagents after the above purification still contained an impurity, which caused two additional peaks in the ^1H NMR spectrum (e.g., for Ln = Yb at δ 0.93 and −1.78). The amount of the impurity appeared to be dependent on the supplier and on the batch. The mass spectra of these reagents showed, in addition to peaks for $Ln(fod)_3$, peaks at higher m/z values. Characteristic were abundant peaks at masses 39 (+K) and 334 (+Kfod) higher than the parent peak for $Ln(fod)_3$. Moreover, the values for the lanthanide-induced shifts, measured with these impure reagents, were much lower than those observed with pure shift reagents; even the relative induced shifts were somewhat different. The latter might be explained by involvement of the impurity in the complexation of the substrate.

We have studied the contamination of the $Yb(fod)_3$ reagent in some detail. Recrystallization from CCl_4 gave a white solid. The mass spectrum of this compound showed important peaks at m/z 1393 and 1098[6] (the calculated mass of $Yb(fod)_3$ is 1059). The 100-MHz ^1H NMR spectrum ($CDCl_3$, 29 °C) showed broad singlets at δ 0.93 and −1.78 (integral ratio 9:1) whereas pure $Yb(fod)_3$ showed peaks at δ 5.23 and −20.61. It can be concluded that the isolated compound is the new binuclear complex $Yb(fod)_3$·Kfod. Comparison of the mass spectra of this compound and that of the crude shift reagent showed that the latter contained—in addition to $Yb(fod)_3$·Kfod—small amounts of the corresponding Na, Rb, and Cs compounds. Analogous phenomena were observed for several other commercial paramagnetic shift reagents (Ln = Dy, Ho, Pr, Eu).

The compound $Yb(fod)_3$·Kfod could be synthesized from $Yb(NO_3)_3 \cdot 5H_2O$ and an excess of Kfod (molar ratio 1:6), using a procedure analogous to that described by Sievers et al. for the preparation of $Yb(fod)_3$.[7]

The K^+ ion in $Yb(fod)_3$·Kfod is exchangeable for other metal ions by shaking a $CHCl_3$ solution of the complex with an aqueous solution of the appropriate metal salt. This can explain the presence of the other alkali ions in the impure shift reagents. Upon exchange for Ag^+ the binuclear complex $Yb(fod)_3$·Agfod was obtained. Mass spectral analysis showed this complex to be identical with the complex prepared[8] according to Sievers et al.,[9] which is reported to be an effective shift reagent for aromatic compounds. Treatment of a solution of $Yb(fod)_3$·Kfod with an aqueous solution of $YbCl_3$ yields $Yb(fod)_3$. This procedure, therefore, is useful for the purification of shift reagents contaminated with $Ln(fod)_3$·Mfod. Alternatively, this purification can be achieved by shaking a $CHCl_3$ solution of the impure shift reagent with 0.1 N HCl to yield a mixture of $Yb(fod)_3$ and Hfod. The latter can be removed by selective adsorption into zeolite NaX or via recrystallization.

Table I. Relative Lanthanide-Induced Shifts[a] in ^1H NMR Spectra of Quinuclidine (1) and Propylamine (2) (2.0 M in CCl_4 at 35 °C)

	H_α[b]	H_β	H_γ
1 + $Yb(fod)_3$·Kfod	1.00	0.50	c
1 + $Yb(fod)_3$	1.00	0.38	c
2 + $Yb(fod)_3$·Kfod	1.00	0.56	0.29
2 + $Yb(fod)_3$	1.00	0.56	0.30

[a] Determined from the slopes of plots of H_β or H_γ vs. H_α. [b] Absolute induced shifts at lanthanide substrate ratio 0.1 are 0.59, 5.22, 15.6 and 15.6, respectively. [c] Not observed due to coincidence with H_β.

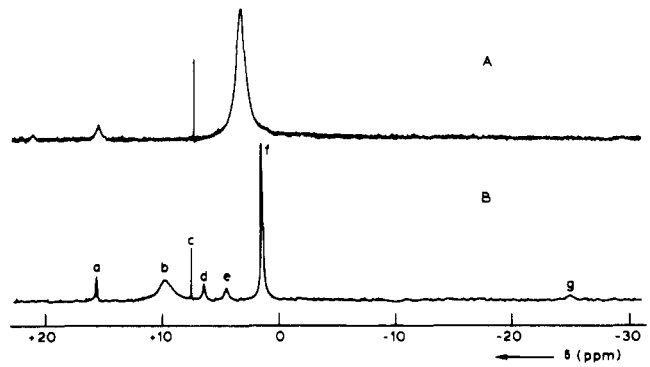

Figure 1. 100-MHz ^1H NMR spectrum of a mixture of 7.2 mg of $Yb(fod)_3$ and 3.4 mg of Hfod in 0.5 mL of $CDCl_3$: (A) at 25 °C; (B) at −27 °C. Assignment: a and d, Hfod (CH's); b, $Yb(fod)_3$ (*t*-Bu); c, $CHCl_3$; e, H[Yb(fod)$_4$] (*t*-Bu); f, Hfod (*t*-Bu); g, $Yb(fod)_3$ (CH).

The complex $Yb(fod)_3$·Kfod induces downfield shifts in the ^1H NMR spectrum of quinuclidine in CCl_4 (see Table I), which are small compared with those obtained with $Yb(fod)_3$. In addition, in the presence of amine, an upfield shift of the *t*-Bu and CH signals of the fod ligands was observed. The relative induced shifts for quinuclidine also differ from those obtained with $Yb(fod)_3$. The magnitude of the relative induced shifts might be explained by coordination of quinuclidine to the K^+ ion in $Yb(fod)_3$·Kfod. Addition of $Yb(fod)_3$·Kfod to a CCl_4 solution of propylamine causes large downfield shifts in the ^1H NMR spectrum of that compound, which are the same as those obtained by using $Yb(fod)_3$ as shift reagent. Mass spectral analysis of the solution obtained[10] showed that $Yb(fod)_3$·Kfod was converted to $Yb(fod)_3(C_3H_7NH_2)_2$ and Kfod. Apparently, the steric demands of propylamine are smaller than those of quinuclidine, allowing an attack of the former on the Yb^{3+} ion.

The present data do not allow definitive conclusions about the structure of $Yb(fod)_3$·Kfod. This complex could consist of a $Yb(fod)_3$ and a Kfod unit, in which two oxygen atoms act as bridging ligands.[11] Other structures, e.g., an anionic complex $K(Yb(fod)_4]$, cannot be excluded. Therefore, an X-ray investigation will be undertaken to establish the structure of the $Yb(fod)_3$·Kfod complex.

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(6) m/z of Yb taken as 174. The characteristic cluster of Yb isotopes was observed.

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(8) Obtained after evaporation of the solvent from a solution of $Yb(fod)_3$ and Ag(fod) in $CHCl_3$, prepared according to ref 9.

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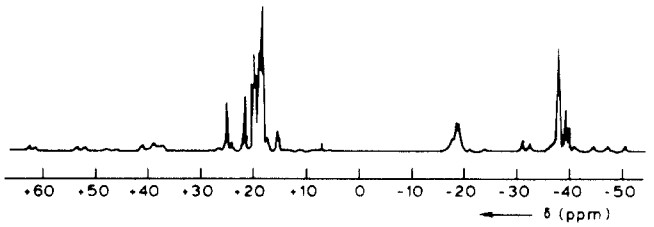

Figure 2. 300-MHz ^1H NMR spectrum of a 0.1 M solution of $Yb(fod)_3$ in $CDCl_3$ at -38 °C.

The existence of an entity in which the Yb^{3+} ion is coordinated by four fod ligands can be deduced from 100-MHz ^1H NMR spectra of mixtures of $Yb(fod)_3$ and the neutral ligand Hfod in $CDCl_3$, which showed at 25 °C a single *t*-Bu signal (Figure 1A). Therefore, at this temperature fast exchange between $Yb(fod)_3$ and Hfod exists. This exchange might take place *via* a complex $H[Yb(fod)_4]$ (eq 1). A decrease of the temperature to -27 °C caused

$$Yb(fod)_3 + Hfod \rightleftharpoons H[Yb(fod)_4] \quad (1)$$

a splitting in the spectrum and then both the $Yb(fod)_3$ and the Hfod signals were observed (Figure 1B). Moreover, small signals at δ 3.66 and 17.1 were present, which might be assigned to the *t*-Bu and CH groups in $H[Yb(fod)_4]$, respectively.

It should be noted that at these temperatures the ligands in $Yb(fod)_3$ as well as in $Yb(fod)_3$·Kfod and $H[Yb(fod)_4]$ give rise to only one *t*-Bu and one CH resonance in the 100-MHz ^1H NMR spectrum. Since at the concentrations used (0.01 M) bimolecular exchange reactions are rather slow, it may be concluded that the fod ligands in these complexes are still rapidly rearranging intramolecularly in such a way that these ligands are effectively magnetically equivalent.[12]

At higher concentrations (0.1 M) the ^1H NMR spectrum of $Yb(fod)_3$ is very complex. At 300 MHz and -38 °C at least 40 peaks were observed (Figure 2), which coalesced at about 115 °C to two broad peaks (*t*-Bu and CH). As the complexity of the spectra appeared to be dependent on the concentration, it seems most likely that these phenomena are due to self-association of $Yb(fod)_3$. Several $Ln(dpm)_3$ shift reagents (dpm = 2,2,6,6-tetramethyl-3,5-heptanedionate) are known to crystallize as dimeric units through sharing of two oxygen atoms by the lanthanide ions.[13] A single dimer structure, however, cannot explain the large number of peaks in the concentrated solution of $Yb(fod)_3$, even when it is assumed that the intramolecular reorientation of the fod ligands and the rotation of the *t*-Bu groups are slow with respect to the NMR time scale. Moreover, the concentration dependence appeared to be inconsistent with a monomer/dimer equilibrium. Therefore, it seems more likely that several dimer configurations and/or oligomers of $Yb(fod)_3$ are present. Anyhow, these results show that in concentrated solutions complex exchange phenomena take place. Since for the evaluation of absolute bound shifts of lanthanide–substrate complexes measurements at a large range of shift reagent/substrate ratios are needed,[14] measurements at high $Ln(fod)_3$ concentrations usually cannot be circumvented. Great care should be taken in the interpretation of these data. On the other hand, the use of relative bound shifts, which usually are obtained from data at low shift reagent/substrate ratios, may lead to other complications.[5a] Probably the best way to determine bound shifts is a direct measurement of these shifts in NMR spectra at low temperatures and high magnetic fields, in which both the shift reagent substrate complex and the free substrate are observed.

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Experimental Section

The 100-MHz ^1H NMR spectra were obtained on a Varian XL-100-15 spectrometer system in the pulse-FT mode. The 300-MHz ^1H NMR spectra were measured on a spectrometer, built at the Department of Applied Physics.[15] Mass spectra were measured on a Varian-Mat 311A spectrometer with a direct insertion probe at temperatures between 50 and 100 °C. All solvents used were dried on zeolite KA prior to use.

$Yb(fod)_3$·Kfod. A solution of 10.67 g of Hfod (36 mmol) in 10 mL of MeOH was neutralized with 9 mL of 4 N KOH. The solution obtained was added to 2.56 g of $Yb(NO_3)_3·5H_2O$ (5.7 mmol) dissolved in a minimal amount of MeOH. The dispersion obtained was added with stirring to 400 mL of H_2O. The white precipitate was filtered to yield 7.72 g of $Yb(fod)_3$·Kfod (5.6 mmol, 98%). Further purification was achieved by recrystallization from CCl_4 at -20 °C; mp 123-124 °C; ^1H NMR ($CDCl_3$) δ 0.93 (br s, *t*-Bu), -1.78 (br s, CH); mass spectrum (70 eV), important peaks at *m/z* 1393 (M), 1374 (M - F), 1354 (M - K), 1098 (M - fod), 1059 ($Yb(fod)_3$), 1002 ($Yb(fod)_3$ - *t*-Bu), 764 ($Yb(fod)_2$), 295 (fod).

Purification of $Yb(fod)_3$ Contaminated with $Yb(fod)_3$·Kfod. A mixture of $Yb(fod)_3$ and $Yb(fod)_3$·Kfod (400.0 mg, ratio about 1:1) was dissolved in 2 mL of CCl_4. The solution obtained was shaken with an aqueous 0.2 M $YbCl_3$ solution (5 × 1 mL) and after that dried on zeolite KA. After evaporation of the solvent and drying under vacuo over zeolite KA, 385.0 mg of $Yb(fod)_3$ was obtained.

Alternatively, the 1:1 mixture could be purified by shaking the CCl_4 solution with 0.1 N HCl (2 × 1 mL). After that the solution was washed with 1 mL of H_2O. Then the Hfod formed was removed quantitatively by treatment of the solution with zeolite NaX. Evaporation of the solvent gave 150 mg of $Yb(fod)_3$. Further purification was obtained by recrystallization from CH_2Cl_2 at -30 °C.

Registry No. 1, 100-76-5; 2, 107-10-8; $Yb(fod)_3$·Kfod, 76927-67-8; $Yb(fod)_3$, 18323-96-1; Hfod, 17587-22-3; $H[Yb(fod)_4]$, 76927-68-9.

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Potential Bile Acid Metabolites. 3.[1] A New Route to Chenodeoxycholic Acid[2]

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In continuation of a program of synthesis of potential bile acid metabolites, a need for a moderate supply of chenodeoxycholic acid (1) prompted us to examine literature preparations of the compound, of which there are several.[4] All of these methods, save one,[5] involve reduction

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(2) 3a,7a-Dihydroxy-5β-cholanic acid. All cholanic acid derivatives mentioned in this work are of the 5β series; the 5β designations are omitted in their names. Chenodeoxycholic acid, one of the "primary" bile acids of higher vertebrates, is used in treatment of gallstones.
(3) On leave, Nihon University, Japan.
(4) (a) L. F. Fieser and S. Rajagopalan, *J. Am. Chem. Soc.*, **72**, 5530 (1950); (b) I. G. Anderson, G. A. D. Haslewood, H. S. Wiggin, and I. D. P. Wotton, *Nature*, **169**, 621 (1952); (c) Y. Sato and N. Ikekawa, *J. Org. Chem.*, **24**, 1367 (1959); (d) E. Hauser, E. Baumgartner and K. Meyer, *Helv. Chim. Acta*, **43**, 1595 (1960); (e) A. F. Hofmann, *Acta Chem. Scand.* **17**, 173 (1963); (f) S. L. Hsia in "The Bile Acids", Vol. I., P. P. Nair and D. Kritchevsky, Eds., Plenum Press, New York, 1971, p 110.

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