680 cm^{-1}, the 668/680 ratio being approximately unity for the 24ξ^1 epimer, less than unity for the 24ξ^2 epimer; (2) absorption beginning below 900 cm^{-1} and a distinct band at 910 cm^{-1} for the 24ξ^1 epimer with no specific absorption at 900 cm^{-1} nor a band at 910 cm^{-1} for the 24ξ^2 epimer; (3) a complex multiplet of bands centered about 930 cm^{-1} for the 24ξ^1 epimer, around 945 cm^{-1} for the 24ξ^2 epimer; and (4) a well-formed doublet at 995 and 1005 cm^{-1}, the 995/1005 ratio being less than unity for the 24ξ^1 epimer, greater than unity for the 24ξ^2 epimer.

Cholest-5-ene-3β,24ξ^1-diol (cerebrosterol) (IIa) was obtained in 53-mg yield from its dibenzoate IIb prepared from IIIa: mp 175° (lit. mp 175–176°,[4] 170–171.5° to 173.5–175°[5d]); $\tilde{\nu}_{max}^{KBr}$ 3400, 1050, 672 cm^{-1}; R_c 0.75 (red-brown color with 50% sulfuric acid); t_R 2.36 (3% QF-1), 2.20 (3% SE-30); identified by direct comparison with authentic samples of cerebrosterol obtained from equine and human brain.

Cholest-5-ene-3β,24ξ^2-diol (IIa). A. From IIIa.—IIa was obtained in 51-mg yield from its dibenzoate IIb: mp 184–186° (lit.[4] mp 182–183°); $\tilde{\nu}_{max}^{KBr}$ 3400, 1050 cm^{-1} (no band at 672 cm^{-1}); R_c 0.75 (red-brown color with 50% sulfuric acid); t_R 2.36 (3% QF-1), 2.20 (3% SE-30).

B. From the 24-Hydroperoxide I.—IIa was obtained previously by borohydride reduction: mp 176–179°; R_c 0.77 (red-brown color with 50% sulfuric acid); identical in infrared and gas chromatogaphic properties with the 3β,24ξ^2-diol prepared under A above; mass spectrum *m/e* 402 (100), 384 (62), 369 (30), 351 (20), 317 (18), 291 (22), 273 (50), 255 (28), etc.

24-Norchol-5-en-3β-ol (IV).—Injection of 5–10 μg of I dissolved in 1–2 μl of chloroform–methanol (9:1) into the flash heater zone (250°) of a Hewlett-Packard F & M Model 402 gas chromatograph and collection of effluxing components in a glass capillary gave IV as the initially eluted component in 14% yield (unidentified component no. 1, 10% yield, in previous studies[8]). The collected sample was homogeneous by thin layer chromatography and by gas chromatography on both 3% QF-1 and 3% SE-30 phases and was characterized: R_c 1.00 (magenta color with 50% sulfuric acid); t_R 0.45 (3% QF-1), 0.38 (3% SE-30); $\tilde{\nu}_{max}^{KBr}$ 3400, 1620, 1060 cm^{-1}. The pure IV was transferred in diethyl ether to a quartz probe and inserted directly into the mass spectrometer to yield the molecular ion at *m/e* 330 (100), 315 (34, M − H_2O), 312 (46, M − CH_3), 297 (48, M − H_2O − CH_3), 273 (28, M − C_4H_9), 255 (37, M − C_4H_9 − H_2O).

3β-Hydroxychol-5-en-24-al (V).—The second component to efflux from the thermally decomposed sample of I was collected in a capillary in 46% yield (unidentified component no. 2, 50% yield previously[8]). The component was homogeneous by thin layer and gas chromatography: R_c 0.85 (magenta-red color with 50% sulfuric acid); t_R 2.40 (3% QF-1), 0.90 (3% SE-30); $\tilde{\nu}_{max}^{KBr}$ 3400, 1720, 1620, 1050 cm^{-1}, identical in these properties with an authentic sample; mass spectrum *m/e* 358 (100, molecular ion), 343 (23), 340 (56), 330 (10), 325 (33), 273 (40, M − C_4H_9O), 255 (20).

3β-Hydroxycholest-5-en-24-one (IIIa).—The third major thermal decomposition product of I was collected in a capillary in 27% yield (unidentified component no. 3, 40% yield previously[8]). The 24-ketone IIIa was homogeneous on thin layer and gas chromatographic analysis: R_c 0.95 (magenta-red color with 50% sulfuric acid); t_R 3.35 (3% QF-1), 1.68 (3% SE-30); $\tilde{\nu}_{max}^{KBr}$ 3400, 1700, 1620, 1060, 1020, 800 cm^{-1}; identical in these properties with an authentic sample; mass spectrum *m/e* 400 (87%, molecular ion), 385 (27), 382 (100), 367 (57), 315 (73), 314 (92), 299 (50), 297 (44), 296 (35), 289 (45), 281 (46), 273 (30, M − $C_8H_{15}O$), 271 (60), 255 (34).

3β-Acetoxycholest-5-en-24-one (IIIb).—Attempted acetylation of I with acetic anhydride–pyridine (1:2) overnight at room temperature in the usual manner resulted in total decomposition of the sterol hydroperoxide (negative peroxide tests). The major product was isolated in 35% yield by preparative gas chromatography, yielding pure IIIb homogeneous on thin layer and gas chromatograms: R_c 1.30 (magenta-red color with 50%, sulfuric acid); t_R 5.9 (3% QF-1); $\tilde{\nu}_{max}^{KBr}$ 1730, 1710, 1380, 1250, 1040 cm^{-1}; identical in these properties with an authentic sample.

Registry No.—I (24*R*), 27460-24-8; I (24*S*), 27460-25-9; IIa (24*R*), 27460-26-0; IIa (24*S*), 27460-27-1; IIb (24*R*), 27460-28-2; IIb (24*S*), 27460-29-3; IIIa, 17752-16-8; IIIb, 20981-59-3; IV, 27460-32-8; V, 27460-33-9.

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The Dieckmann Cyclization as a Route to *A*-Nor Steroids. Evidence Concerning Stereochemistry

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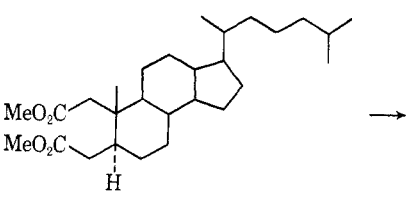
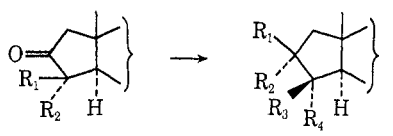
The successful preparation of a β-keto ester by the Dieckmann cyclization as a synthetic route to an *A*-nor steroid was first reported by Fuchs and Loewenthal in the cholestane series.[2] This synthesis was noteworthy for its specificity; of four possible isomers, with the carbomethoxyl substituted at either the 1 or 3 carbon with an α or β configuration, only one compound formed. The product was formed from the requisite diester, dimethyl 2,3-*seco*-5α-cholestan-2,3-dioate (**2**) (Scheme I), by treatment with potassium *tert*-butoxide in refluxing benzene.

SCHEME I



2



1a, $R_1 = CO_2Me$; $R_2 = H$
b, $R_1 = H$; $R_2 = CO_2Me$

3a, $R_1 = R_4 = H$; $R_3 = CO_2Me$; $R_2 = OH$
b, $R_2 = R_3 = H$; $R_4 = CO_2Me$; $R_1 = OH$

The original choice of configuration was made in favor of **1a** rather than **1b** for two reasons. It was shown that in the sodium borohydride reduction product, the hydroxy ester **3**, the hydroxyl and carbomethoxyl groups were trans with respect to one another. Then, by application of Klyne's principle of enantiomeric types,[3] the hydroxyl group was assigned as α; by inference, the carbomethoxyl group was β, and the structure was assigned as **3a**.

(1) (a) Abstracted in part from the M.S. thesis of B. V. P., Miami University, 1969. (b) Presented in part at the 2nd Central Regional Meeting of the American Chemical Society, Columbus, Ohio, June 3–5, 1970.
(2) B. Fuchs and H. Loewenthal, *Tetrahedron*, **11**, 199 (1960).
(3) W. Klyne, *J. Chem. Soc.*, 2916 (1952).

The possibility that the correct assignment for the β-keto ester is **1b** has been suggested by Smith,[4] by application of Karplus' rules to the coupling of the C-3 proton with the 5α H. The observed coupling constant is 13 cps which is consistent with the dihedral angle between the two protons such that the protons are trans, which places the carbomethoxyl group in the α configuration.

It is the purpose of this paper to examine other evidence arising particularly from the solvent effects on the C-19 proton-singlet chemical shift and from ORD studies of **1**, **3**, and other relevant compounds as it relates to the question of the stereochemistry. We also describe the preparation of the requisite compounds.

Wenkert, *et al.*,[5] have observed an empirical correlation of configuration and solvent effects on comparative chemical shifts in $CDCl_3$ and pyridine-d_5. By analysis of a large number of spectra, certain generalizations were formulated. One of these related to the interaction of a hydroxyl group 1,3 cis or trans to a methyl or hydrogen in a six-membered ring. Deshielding of the chemical shift of the latter of 0.20–0.40 ppm in pyridine relative to $CDCl_3$ was observed when a 1,3-cis diaxial orientation was present, a distinct departure from the normal shielding observed for most systems in pyridine. Less extensive evidence in their investigation suggests that the correlation also operates in five-membered rings. This represented a possible method to distinguish the configuration **3a** postulated for the hydroxy ester by Fuchs and Loewenthal and its isomer **3b**, since a substantial deshielding should be found for the C-19 singlet in the latter case but not the former. Since other orientations are precluded, one could deduce the configuration of the β-keto ester **1**.

The observed C-19 chemical shifts and Δ values ($\Delta = \delta_{CDCl_3} - \delta_{pyr}$) are given in Table I.

TABLE I

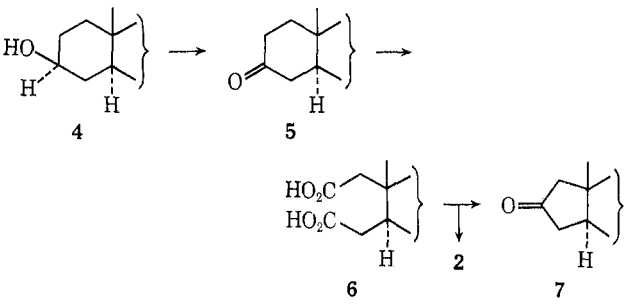
PMR C-18 AND C-19 CHEMICAL SHIFTS[a]

	C-19			C-18		
Compd	$CDCl_3$	Pyr-d_5	Δ	$CDCl_3$	Pyr-d_5	Δ
6	0.84			0.68		
2	0.81			0.65		
1	0.87	0.75	+0.12	0.67	0.63	+0.04
3	0.97	1.17	−0.20	0.68	0.68	0.00
7	0.83	0.73	+0.10	0.68	0.64	+0.04

[a] In ppm.

The Δ value of **3** supports a β configuration for the hydroxyl group. The fact that only a small change, 0.12 ppm upfield, is observed for the β-keto ester in pyridine and that this difference is similar to Δ for the ketone **7** (Scheme II) lends credence to the hypothesis that the carbomethoxyl function is α, since its presence appears not to affect solvation above the A ring. A recent example of a 1,3 methyl–carbomethoxyl group interaction reports δ 0.83 ppm (in $CDCl_3$) for the CH_3 signal when the groups are trans, and δ 0.95 ppm for the cis configuration.[6] The trans value is nearly the same as that for **1**.

SCHEME II



Further, one can compare reported chemical shifts in $CDCl_3$ observed for the hydroxyl ester **3** and the β-keto ester **1** with known *A*-norcholestan-2-ol derivatives. Conversion of the *A*-nor ketone **7** to the 2β-hydroxy compound leads to a shift downfield of 0.07 ppm in the C-19 signal; the 2α-hydroxy methyl signal is shifted upfield 0.17 ppm. Likewise in the androstane series, the effect of 16-ketone-to-alcohol conversions on the C-18 signal is 0.05 downfield for the β-OH case and 0.18 upfield in the α-OH case.[7,8] Thus, the effect of the 1,3-cis hydroxyl function appears consistently to support a deshielding of 0.05 to 0.15 ppm, for the methyl signal consistent with our assignment for the configuration of these products.

The ORD curves for **7** and the β-keto ester **1b** show positive Cotton effects centered at 300 nm. The amplitudes are, respectively, +228 and +283, so that the effect of the carbomethoxyl group is to enhance the Cotton effect observed for the ketone. This enhancement is consistent with the presence of the carbomethoxyl group in either the lower right rear octant or top right forward octant as they are structured with respect to the carbonyl nodal planes. Inspections of models of the β-keto ester show that an α configuration places the functional group in the proper lower right rear octant; however, for the β configuration the group falls in the upper right rear octant which would lead to a prediction of diminution of the magnitude of the Cotton effect as compared with the *A*-nor ketone **7**. The application of the octant rule has been used for purposes of stereochemical assignment in cases of rigid cyclopentanone systems such as **1b**.[9]

The synthetic sequence leading to the requisite compounds for this study is shown in Scheme II. The preparations in general followed methods previously reported.

Experimental Section

Melting points were determined on a Thomas-Hoover melting point apparatus and are corrected. Analytical samples were recrystallized to constant melting points, and microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Ir spectra were determined on a Perkin-Elmer Model 237B spectrometer and uv spectra by a Cary Model 14 recording spectrophotometer. Nuclear magnetic resonance spectra were recorded in external lock mode on a Jeolco C-60H spectrometer at

(4) A. H. Smith, Ph.D. Thesis, 1968, Brown University, Providence, R. I.; *Diss. Abstr. B*, **30**, 139 (1969).

(5) P. V. DeMarco, E. Farkas, D. Doddrell, B. L. Mylari, and E. Wenkert, *J. Amer. Chem. Soc.*, **90**, 5480 (1968).

(6) M. E. Kuehne, *J. Org. Chem.*, **35**, 171 (1970).

(7) J. Jacques, M. Minssen, and D. Varech, *Bull. Soc. Chim. Fr.*, **32**, 77 (1965).

(8) D. Williams and N. Bhacca, *Tetrahedron*, **21**, 1641, 2021 (1965).

(9) A. K. Bosey, *Tetrahedron Lett.*, 461 (1961); P. Crabbe, A. Cruz, and and J. Iriarte, *Can. J. Chem.*, **46**, 349 (1968); A. R. VanHorn and C. Djerassi, *J. Amer. Chem. Soc.*, **89**, 651 (1967).

60 MHz, using 30–35 mg of steroid per 0.6 ml of solvent, either $CDCl_3$ or pyridine-d_5, and TMS as internal standard. The methyl signals of the cholestane side chain at C-21 and C-26,27 were centered at 0.84 ± 0.02 ppm, respectively, each with J = 6–8 cps for all compounds reported in both solvents. The assignment of these bands and the C-19 signal was based on the coupling constants and the relative peak intensities. Mass spectra were determined on an Hitachi RMU-6B single-focusing mass spectrometer. ORD curves were recorded on a Jasco 5A spectropolarimeter. The authors are indebted to Dr. R. B. Treptow and to Procter and Gamble, Co., Miami Valley Laboratories, for the use of their spectropolarimeter.

Oxidation of 5α-Cholestan-3β-ol (4) to 5α-Cholestan-3-one (5) by Jones Reagent.—5α-Cholestan-3-one (**5**) was prepared as previously described.[10] The ketone was recrystallized from acetone: mp 128–128.5°; $[\alpha]D$ +44.4° (*c* 4.27, $CHCl_3$) (lit.[11] mp 129°; $[\alpha]D$, +42–44°); ir (KBr) 1709 cm^{-1}; nmr ($CHCl_3$) δ 1.00 s (19-CH_3), 0.65 s (18-CH_3) (lit.[12] δ 1.01, 0.67).

2,3-*seco*-5α-Cholestan-2,3-dioic acid (6) was prepared according to the method of Rull and Ourisson.[13] After adding a solution of the ketone **5** (6.00 g, 13.8 mmol) in 120 ml of glacial acetic acid to CrO_3 (5.54 g, 55.4 mmol) suspended in 100 ml of HOAc at 70°, the reaction mixture was maintained at 85° for 26 hr. Subsequent work-up gave **6**: 4.60 g (68%); mp 194.5–195° (EtOAc), $[\alpha]D$ +35.5° (*c* 0.013) (lit.[14] mp 195–196°; $[\alpha]D$ +35.7°; ir (KBr) 3700–3100 (OH), 1705 (C=O), 925 cm^{-1} (diacid); nmr ($CDCl_3$) δ 0.68 s (18-CH_3), 0.84 s(19-CH_3), 8.2–10.7 s (COOH).

Dimethyl 2,3-*seco*-5α-cholestan-2,3-dioate (2) was prepared by methylation by a method analogous to that of Ourisson[15] except that *N*-nitroso-*N*-methyl-*p*-toluenesulfonamide (Diazald, Aldrich Chemical Co., Milwaukee) was used as a CH_2N_2 precursor. The reaction gave **2** which was recrystallized (MeOH): mp 59–60°, $[\alpha]D$ +23.5° (lit.[16] mp 59–60°; $[\alpha]D$ +20°); ir (KBr) 1745 cm^{-1} (C=O ester); nmr ($CDCl_3$) δ 0.81 s (19-CH_3), 0.65 s (18-CH_3), 3.67 s ($COOCH_3$); mass spectrum (70 eV) *m/e* (rel intensity) 464 (1), 428 (2), 380 (24).

3α-Carbomethoxy-*A*-nor-5α-cholestan-2-one (1b) was prepared according to the method of Fuchs and Loewenthal[2] except that the solvent contained benzene and DMSO in a ratio of 5:1 by volume. The product gave the following data: mp 108–109°; $[\alpha]D$ +111° (*c* 0.10, $CHCl_3$) (lit.[2] mp 110–111°; $[\alpha]D$ +109°); ir 3700–3200 weak (enol OH), 1765 (cyclopentanone C=O), 1727 cm^{-1} (ester C=O); uv max (EtOH) 294 nm (ε 4.25); nmr ($CDCl_3$) 0.68 s (18-CH_3), 0.87 s (19-CH_3), 3.73 s (methyl ester), 3.08 d (C-3, J = 13 Hz); nmr (pyr) 0.75 s (19-CH_3), 0.63 s (18-CH_3); ORD (*c* 0.10, MeOH) Φ × 10^{-3} (nm), +3.66 (375), +10.52 (335), +16.55 (326), +14.82 (321), +16.32 (316), +5.80 (305), 0 (300), −12.03 (278), −10.54 (255); a +283; mas spectrum (70 eV) *m/e* (rel intensity) 430 (62), 415 (46, M − CH_3), 399 (34, M − CH_3O), 275 (105).

3α-Carbomethoxy-*A*-nor-5α-cholestan-2β-ol (3b) was prepared by reduction of **1b** as previously described.[2] The crude product recovered was chromatographed on neutral alumina and gave **3b**: mp 119–122.5° (lit.[2] 121.5–122.5°); ir 3500 (broad, OH), 1728 cm^{-1} (C=O, ester); nmr ($CDCl_3$) 0.68 s (18-CH_3), 0.97 s (19-CH_3); nmr (pyr) 1.17 s (19-CH_3), 0.68 s (18-CH_3).

***A*-Nor-5α-cholestan-2-one (7)** was prepared from the diacid **6** by the method of Castells, *et al.*[17] The crude product recovered gave **7**: mp 96–97° (lit.[17] 101–102°); ir (KBr) 1745 (cyclopentanone C=O); uv (MeOH) 237.5 nm (ε 253), 297.5 (97); nmr ($CDCl_3$) δ 0.65 s (18-CH_3), 0.83 s (19-CH_3); nmr (pyr) δ 0.64 (18-CH_3), 0.73 (19-CH_3); mass spectrum (70 eV) *m/e* (rel intensity) 372 (6.8), 357 (2.61), 202 (1.11), 214 (1.0); ORD (*c* 0.10, MeOH) Φ × 10^{-3} (λ, nm) +2.64 (375), +4.38 (350), +10.69 (325), +10.57 (322), +12.20 (315), +7.85 (308), +5.00 (302), 0 (297.5), −8.53 (285), −10.57 (275), −8.53 (2.60); a +228 (lit.[18] +234).

Registry No.—**1b**, 27460-19-1; **2**, 1180-24-1; **3b**, 30157-81-4; **4**, 80-97-7; **6**, 1178-00-3; **7**, 2310-36-3.

(10) A. Bowers, T. Halsal, E. Jones, and A. Lemin, *J. Chem. Soc.*, 2548 (1953).

(11) O. Diels and E. Abderhalden, *Ber.*, **39**, 884 (1906).

(12) P. C. Cherry, R. T. Cottrell, G. D. Meakins, and E. E. Richards, *J. Chem. Soc. C*, 181 (1967).

(13) T. Rull and G. Ourisson, *Bull. Soc. Chim. Fr.*, 1573 (1958).

(14) B. H. Brown, I. M. Heilbron, and E. R. H. Jones, *J. Chem. Soc.*, 1482 (1940).

(15) A. Giroud, A. Rassat, P. Witz, and G. Ourisson, *Bull. Soc. Chim. Fr.*, 3240 (1964).

(16) B. B. Smith and H. R. Nace, *J. Amer. Chem. Soc.*, **76**, 6119 (1954).

(17) J. Castells, G. Fletcher, E. Jones, G. Meakins, and R. Swindells, *J. Chem. Soc.*, 2627 (1960).

(18) W. Klyne, *Tetrahedron*, **13**, 29 (1961).

The Thienylfurans

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The scope and limitations of the photochemically induced valence bond isomerization has been reasonably well defined.[1-3] Nevertheless a number of intriguing questions remain particularly in the area of heteroaromatic-substituted thiophenes.[2]

This note describes the synthesis of the four isomeric thienylfurans (**1**,[3a] **2**,[3a] **3**, and **4**) and preliminary irradiation experiments (Scheme I).

2-(2-Thienyl)furan (**1**), a straw-colored oil, bp 46–47° (17 mm), was prepared in 20% overall yield starting with ethyl-2-thenoylacetate (**5**).[4] The latter (**5**) was condensed with α,β-dichloroethyl ethyl ether,[5] and the ester **6** thus formed could be hydrolyzed and decarboxylated to **1**.

3-(2-Thienyl)furan (**2**), 2-(3-thienyl)furan (**3**), and 3-(3-thienyl)furan (**4**) were prepared by a route developed earlier by us for the synthesis of 2,3-diethienyl,[6] 3-phenylfuran,[7] and 3,3′-difuryl.[8] The starting materials **7**, **11**, and **15** have been described previously,[9-11] while the ketones **8** and **12** are also available by tested procedures.[7,12,13] Dehydration of the carbinols **9**, **13**, and **16** was carried out *in situ*[10,11] by distillation from dilute sulfuric acid. In each case a mixture of bond isomers, the thienyldihydrofurans **10**, **14**, and **17**, was ob-

(1) (a) H. Wynberg, R. M. Kellogg, H. van Driel, and G. E. Beekhuis *J. Amer. Chem. Soc.*, **89**, 3501 (1967); (b) R. M. Kellogg, J. K. Dik, H. van Driel, and H. Wynberg, *J. Org. Chem.*, **35**, 2737 (1970).

(2) H. Wynberg, T. J. van Bergen, and R. M. Kellogg, *ibid.*, **34**, 3175 (1969).

(3) R. M. Kellogg, T. J. van Bergen, and H. Wynberg, *Tetrahedron Lett.*, 5211 (1069).

(3a) NOTE ADDED IN PROOF.—It has just come to my attention that D. J. Klinke [Dissertation Abstracts, University Microfilms, Inc., Ann Arbor, Mich., 1964; Ph.D. Thesis, University of Michigan, 1963 (thesis director Dr. R. D. Schuetz)] described the synthesis and several reactions of **1** and **2**. The physical properties agree.

(4) R. Levine and C. R. Hauser, *Tetrahedron Lett.*, **66**, 1768 (1944).

(5) F. Reichstein, A. Grusssner, and H. Tschokke, *Helv. Chim. Acta*, **15**, 1066 (1932).

(6) H. Wynberg, A. Logothetis, and D. Verploeg, *J. Amer. Chem. Soc.*, **79**, 1972 (1957).

(7) H. Wynberg, *ibid.*, **80**, 364 (1958).

(8) H. Wynberg and J. W. van Reijendam, *Recl. Trav. Chim. Pays-Bas*, **86**, 381 (1967).

(9) H. Gilman and D. A. Shirley, *J. Amer. Chem. Soc.*, **71**, 1870 (1949).

(10) S. Gronowitz, *Ark. Kemi*, **7**, 361 (1954).

(11) V. Ramananthan and R. Levine, *J. Org. Chem.*, **27**, 1216 (1962).

(12) Yu. K. Yur'ev, I. K. Korobitsyna, and L. A. Savina, *Dokl. Akad. Nauk SSSR*, **86**, 91 (1952) [*Chem. Abstr.*, **47**, 7478 (1953)]; J. H. S. Weiland, H. Dijkstra, and A. B. Pik, *Recl. Trav. Chim. Pays-Bas*, **82**, 651 (1963).

(13) P. Karrer and A. Kiese, *Helv. Chim. Acta*, **27**, 1285 (1945); R. B. Woodward and R. H. Eastman, *J. Amer. Chem. Soc.*, **68**, 2229 (1946). The most convenient preparation of ketone **12** consists of pyrolysis of the barium salt of 3-thiaadipic acid at 230° using the method developed by R. M. Acheson, J. A. Barltrop, H. Hichens, and R. F. Hichens, *J. Chem. Soc.*, 650 (1961), for alkylsubstituted thiaadipic acids. See also F. A. Buiter, *Diss.*, Groningen (Holland), 1966.