C-10, C-12, C-14, and C-16. Incorporation of eight intact acetate units in the polyketide chain was indicated by analysis of the derivative (1c) obtained from feeding experiments with [1,2-$^{13}C_2$]acetate. Although the long relaxation times of some of the carbon atoms and the overlap of certain signals precluded the complete determination of all the carbon–carbon coupling constants, the available data were consonant with a polyketide pathway with the chain extending from C-16 through the ring systems to C-1, in the direction of decreasing numbers of the carbon atoms as shown in the Scheme I.

The only remaining ambiguity in the structural elucidation of actinorhodin, viz., whether the two monomeric units are connected at C-9 or at C-10, could be neatly resolved from the biosynthetic enrichment studies. The only sp^2 carbon atom bearing a directly bonded hydrogen atom arises from C-1 of acetate, thus identifying it as C-9 and placing the point of dimerization at C-10. The same conclusion has been reached by Zeeck and co-workers[10] on purely chemical grounds.

Experimental Section

^{13}C NMR spectra were recorded on Varian FT-80, JEOL PFT-100, and Nicolet NT-360 spectrometers. The spectra were generally recorded at a repetition time of 5 s from a 90° pulse, using $CDCl_3$ as solvent.

Incorporations of Sodium [1-^{13}C]-, [2-^{13}C]- and [1,2-$^{13}C_2$]-Acetates. Preliminary experiments on cultures of *Streptomyces coelicolor* A3(2) grown in shake cultures (300 rpm) at 28 °C on complete medium[11] showed that actinorhodin production reached a maximum on the tenth day after inoculation.

To each of eight 500-mL Erlenmeyer flasks containing the 4-day-old growth of *Streptomyces coelicolor* on the complete medium (150 mL) was added [1-^{13}C]-, [2-^{13}C]-, or [1,2-$^{13}C_2$]acetate (1 g; 90% enriched) in portions every 24 h from day 4 to day 7. After 10 days the cultures were filtered, and the mycelium was washed with hydrochloric acid (0.1 N, 2 L) and stirred with 2 N hydrochloric acid (100 mL) for 2 h and then with acetone (100 mL) for 30 min. The residue was filtered, dried, and stirred with sodium hydroxide (2 N, 100 mL). After filtration the filtrate was acidified with hydrochloric acid (2 N). The crude actinorhodin obtained on centrifugation was dried in vacuo. A typical yield was 640 mg.

Actinorhodin Dimethyl Ester Tetraacetate (1c). The crude finely powdered actinorhodin obtained above was suspended in methanol–dioxane (1:1 v/v, 200 mL). Dry hydrogen chloride was bubbled through the suspension until saturation, and the resulting mixture refluxed for 3 h. The solvent was removed under reduced pressure and the residue partitioned between chloroform and water. The chloroform layer was dried (Na_2SO_4) and the solvent removed under reduced pressure. The crude actinorhodin dimethyl ester (1b) was dissolved in acetic anhydride–pyridine (1:2 v/v, 15 mL) and left at 20 °C for 24 h. The solution was poured into water (150 mL) and extracted with chloroform (2 × 50 mL). The chloroform layer was dried (Na_2SO_4) and the solvent removed under reduced pressure. Purification by chromatography on silica gel, eluting with chloroform–methanol (95:5 v/v), and crystallization from benzene gave actinorhodin dimethyl ester tetraacetate (1c) (40 mg) as yellow needles, whose identity was confirmed by comparison of its properties with the published data.[3]

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Registry No. 1a, 15428-92-9; 1c, 15429-00-2.

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Synthesis of Calcitroic Acid, a Metabolite of 1α,25-Dihydroxycholecalciferol[1]

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1α,25-Dihydroxyvitamin D_3 (1α,25-$(OH)_2D_3$) is the most potent known metabolite in the vitamin D series for the regulation of calcium and phosphate homeostasis.[2] Recently it was discovered that rats rapidly metabolize 1,25-$(OH)_2D_3$ to a compound having an acid function on the side chain.[3] This metabolite was isolated as the methyl ester and identified as methyl 1α,3β-hydroxy-24-nor-9,10-secochola-5,7,10(19)-trien-23-oate or calcitroic acid methyl ester.[3] The synthesis of **1a** was of interest to confirm the structure of the biologically generated compound and to provide a route for obtaining a sufficient quantity of the metabolite for examining its biological activity. A convenient synthetic route yielding **1** and a comparison of spectral and chromatographic properties of synthetic and biologically generated **1b** are presented herein.

By use of the general method of Ryer and Gebert,[4] an Arndt–Eistert homologation sequence starting with commercially available **2** provided the side chain desired in the final product. Use of methanol in the silver oxide catalyzed Wolff rearrangement directly yielded the methyl ester, **3**, which was recovered in approximately 60% yield after recrystallizations; **3** was converted to the 5,7-diene, **4a**, by allylic bromination and dehydrobromination.[5,6] Retention of configuration at C-20 is expected[7] and was confirmed by 270-MHz NMR spectra. Mild hydrolysis yielded **4b** which was purified and irradiated to form previtamin **5**. After separation from the other photoisomers by high-pressure liquid chromatography (high-pressure LC), **5** was thermally isomerized to vitamin D ester **6**.

Introduction of the 1α-hydroxy function was achieved by the method fo Paaren et al.[8] Intermediate **6** was converted to the 3,5-cyclovitamin **7** by bicarbonate-buffered methanolysis of the 3-tosylate.[9] Allylic oxidation of **7** with selenium dioxide and *tert*-butyl hydroperoxide in dichloromethane[8] gave the desired 1α-hydroxy derivative. Cycloreversion of the oxidized cyclovitamin with glacial acetic acid gave **1c**, which after high-pressure LC purification, was hydrolyzed to **1b**. This compound was fully characterized and used for comparison with the methylated biological metabolite. Vigorous alkaline hydrolysis yields the natural product, **1a**, for use in biological testing.

Synthetic **1b** demonstrated UV and mass spectra identical with those found for the methyl ester of the isolated metabolite[3] and was found to comigrate with the biological material in analytical high-pressure LC. These findings

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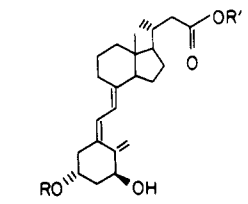
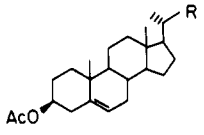
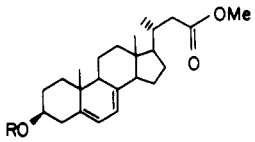


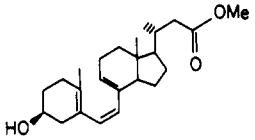
1 a R=H, R'=H
b R=H, R'=Me
c R=Ac, R'=Me



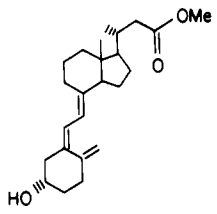
2 R=COOH
3 R=CH_2 COOMe



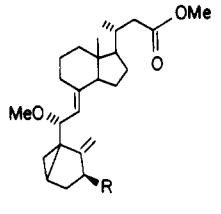
4 a R=Ac
b R=H



5



6



7 R=H
8 R=OH

confirm the structure proposed by Esvelt et al.[3] and establish the hydroxyl configurations as 1α and 3β. Thus the structure of this major metabolite of 1,25-$(OH)_2D_3$ was confirmed to be 1α,3β-dihydroxy-24-nor-9,10-seco-5,7,10-(19)-cholatrien-23-oic acid, **1a**.

Experimental Section

NMR spectra were taken in $CDCl_3$ with a Bruker WH-270 FT spectrometer. Mass spectra were obtained at 110–120 °C above ambient temperature at 70 eV with an AEI MS-9 spectrometer coupled to a DS-50 data system. Ultraviolet (UV) absorption spectra were recorded in methanol with a Beckman Model 24 recording spectrophotometer. High-pressure LC was performed on a Waters Associates Model ALC/GPC 204 using a Zorbax-SIL (Du Pont) 6.4 mm × 25 cm or 4.8 mm × 25 cm column, monitoring at 313 nm for preparative samples or 254 nm for analytical samples. Liquid scintillation counting of radioactivity was determined with a Packard Model 3255 using a scintillation solution consisting of 0.4%, 2,5-diphenyloxazole and 0.03% dimethyl-1,4-bis[2-(5-phenyloxazolyl)]benzene in toluene. All reactions were carried out under a nitrogen atmosphere.

Methyl 3β-Acetoxy-24-nor-5-cholen-23-oate (3). A solution of 5 g (12.3 mmol) of **2** in 10 mL of freshly distilled thionyl chloride was stirred at 25 °C for 90 min. Excess thionyl chloride was removed by distillation after 5 additions of 20 mL of benzene. The brown residue was suspended in 50 mL of benzene and slowly added to a 130-mL ether solution containing approximately 2 g of diazomethane (2-fold excess) at 0 °C. The reaction mixture was left at room temperature for 18 h, resulting in the formation of pale yellow crystals. Solvents were evaporated and the crude diazo ketone, dissolved in 50 mL of benzene and 110 mL of methanol, was heated to 60 °C and suspension of 6 mmol of silver oxide in 50 mL of methanol was added slowly. After the mixture was refluxed at 70 °C for 20 h, the solvents were evaporated and the residue (taken up in ether) was filtered through Celite. The ether solution was adjusted to 100 mL, washed with 0.1 N HCl, dilute $NaHCO_3$, and water, and dried over sodium sulfate. The methyl ester product, **3**, was recrystallized from 10% acetone in methanol and 100% ethanol to give 3.2 g (60%) of white needles: mp 126.0–127.5 °C (lit.[4] mp 125–129 °C); mass spectrum, *m/e* (relative intensity) 356 (100, M^+ – HOAc), 341 (29), 325 (2.4), 282 (4.5), 255 (24); NMR δ 0.66 (s, 3 H, 18-CH_3), 0.93 (d, 3 H, 21-CH_3), 0.97 (s, 3 H, 19-CH_3), 2.01 (s, 3 H, OAc), 2.27 (d, 2 H, 22-CH_2), 3.60 (s, 3 H, 23-$COOCH_3$), 4.5 (m, 1 H, 3α-H), 5.33 (m, 1 H, 6-H).

Methyl 3β-Hydroxy-24-norchola-5,7-dien-23-oate (4b). To a solution of **3** (500 mg, 1.2 mmol) in 22 mL of benzene and 17 mL of hexane was added 500 mg of $NaHCO_3$ and 1.5 equiv of 1,3-dibromo-5,5-dimethylhydantoin. The reaction mixture was refluxed at 75 °C for 20 min, then rapidly cooled, and filtered. The residue obtained upon solvent evaporation was dissolved in 17 mL of xylene and 4 mL of *S*-collidine and reluxed for 90 min. Ether was added and the organic phase was thoroughly washed with 1 N HCl, dilute $NaHCO_3$, water, and saturated NaCl and then dried over Na_2SO_4. The residue (containing 5,7- and 4,6-diene products) was heated in dry dioxane with 80 mg of *p*-toluenesulfonic acid at 70 °C for 45 min. The mixture was diluted with ether and washed with water, dilute bicarbonate, water, and saturated NaCl. The dried residue was chromatographed on a silica gel column (2 × 15 cm) eluted with 15% EtOAc in hexane. The product (**4a**) eluting between 51 and 102 mL obtained in 29% yield from **3** was stirred in 10 mL of ether and 10 mL of 5% (w/v) KOH in 95% methanol for 30 min at room temperature. The reaction mixture was diluted with ether and the organic phase was washed as above. The product was purified on TLC (40% EtOAc in hexane, developed twice, R_f 0.33) to give 96 mg of **4b** (21% from 3): UV λ_{max} 282 nm (ϵ, 11 800), 272 (11 200); high-resolution mass spectrum, calcd for $C_{24}H_{36}O_3$ 372.2664, found 372.2652; mass spectrum, *m/e* 362 (M^+, 100), 339 (60), 313 (30), 143 (40), 104 (90); NMR δ 0.66 (s, 3 H, 18-CH_3), 0.94 (s, 3 H, 19-CH_3), 1.01 (d, 3 H, 21-CH_3), 3.67 (s, 3 H, 23-$COOCH_3$), 2.76 (m, 1 H, 3α-H), 5.39 (d, J = 6.2 Hz, 1 H, 7-H), 5.56 (d, J = 6.2 Hz, 1 H, 6-H).

Methyl 3β-Hydroxy-24-nor-9,10-secochola-5,7,10(19)-trien-23-oate (6). Ether solutions of approximately 20 mg of **4b** were irradiated on ice and under nitrogen for 10 min with a mercury arc lamp (Hanovia 9A-1) fitted with a Corex filter. The residues obtained after solvent evaporation were chromatographed on high-pressure LC (6.4 mm × 25 cm Zorbax-SIL, 4 mL/min, 1500 psi) eluted with 1.5% 2-propanol in hexane. Pure previtamin, **5**, was collected at 45 mL (UV λ_{max} 260 nm, λ_{min} 231 nm). The previtamin product from five separate irradiations was combined and heated in 10 mL of ethanol at 80 °C for 150 min to yield 10.8 mg of **6** (11% yield from 4): UV λ_{max} 264 nm (ϵ, 17 800); high-resolution mass spectrum, calcd for $C_{24}H_{36}O_3$ 372.2664, found 372.2661; mass spectrum, *m/e* (relative intensity) 372 (44), 354 (3), 341 (6), 313 (4), 298 (1), 271 (4), 253 (7), 136 (97), 118 (100); NMR δ 0.58 (s, 3 H, 18-CH_3), 0.99 (d, J = 5.9 Hz, 3 H, 21-CH_3), 3.67 (s, 3 H, 23-$COOCH_3$), 3.95 (m, 1 H, 3α-H), 4.81 (s, 1 H, 19(*Z*)-H), 5.05 (s, 1 H, 19(*E*)-H), 6.03 (d, J = 10.6 Hz, 1 H, 7-H), 6.23 (d, J = 10.6 Hz, 1 H, 6-H).

Methyl 1α,3β-Dihydroxy-24-nor-9,10-seco-5,7,10(19)-cholatrien-23-oate (Calcitroic Acid Methyl Ester, 1b). A solution of **6** (10.2 mg, 27 μmol) in pyridine (0.2 mL) was treated with 30 mg of *p*-toluenesulfonyl chloride at 4 °C for 22 h. After addition of dilute bicarbonate (2 mL) the product was extracted with $CHCl_3$–ether (10 mL); the combined organic phases were washed with 1 N HCl, dilute bicarbonate, water, and saturated NaCl and dried over $MgSO_4$; NMR δ 0.57 (s, 3 H, 18-CH_3), 0.99 (d, J = 5.9 Hz, 3 H, 21-CH_3), 2.45 (s, 3 H, tosyl-CH_3), 3.66 (s, 3 H, 23-$COOCH_3$), 4.68 (m, 1 H, 3α-H), 4.81 (s, 1 H, 19(*Z*)-H), 5.03 (s, 1 H, 19(*E*)-H), 5.96 (d, J = 10.6 Hz, 1 H, 7-H), 6.09 (d, J = 10.6 Hz, 1 H, 6-H), 7.40 and 7.85 (m, 4 H, $RC_6H_4SO_3R$). The 3-tosyl derivative was then solvolyzed in 0.3 mL of benzene, 2 mL of methanol, and 50 mg of $NaHCO_3$ by heating to 56 °C for 18 h. The resulting cyclovitamin product (**7**) was extracted into ether, washed with water and saturated NaCl, dried, and purified on silical gel TLC (30% EtOAc/hexane, R_f 0.54) in 79% yield from **6**: mass spectrum, *m/e* 386 (M^+, 15), 344 (45), 253 (15), 235 (18), 118 (60); NMR δ 0.57 (s, 3 H, 18-CH_3), 0.74 (m, 1 H, 4-H), 0.99 (d, J = 5.9 Hz, 21-CH_3), 3.26 (s, 3 H, 6-OCH_3), 3.66 (s, 3 H, 23-$COOCH_3$), 4.15 (d, J = 9.2 Hz, 1 H, 6-H), 4.88 (s, 1 H, 19(*Z*)-H), 4.99 (d, J = 9.2 Hz, 1 H, 7-H), 5.04 (s, 1-H, 19(*E*)-H). This product in 0.7 mL of CH_2Cl_2 was then added to an ice-cooled solution containing 0.5 equiv of SeO_2 and 2 equiv of *t*-BuOOH in 0.5 mL of CH_2Cl_2.[8] The reaction, followed by TLC, was allowed to proceed at room temperature for a total of 40 min and was stopped with the addition of $NaHCO_3$ and ether. The organic phase was washed with dilute bicarbonate, water, and saturated NaCl and dried over

$MgSO_4$. Evaporation of solvent and purification gave 1α-hydroxy derivative 8, in 50% yield: mass spectrum, m/e 402 (M^+, 40), 370 (70), 329 (35), 235 (45), 135 (100); NMR δ 0.57 (s, 3 H, 18-CH_3), 0.64 (m, 1 H, 4-H), 0.99 (d, J = 5.9 Hz, 21-CH_3), 3.26 (s, 1 H, 6-OCH_3), 3.66 (s, 3 H, 23-$COOCH_3$), 4.17 (d, J = 8.9 Hz, 1 H, 6-H), 4.22 (m, 1 H, 1β-H), 4.96 (d, J = 8.9 Hz, 1 H, 7-H), 5.16 (s, 1 H, 19(*Z*)-H), 5.24 (s, 1 H, 19(*E*)-H). The 1α-hydroxycyclovitamin 8 was dissolved in 0.5 mL of glacial acetic acid and heated at 55 °C for 15 min. Products (1c and the corresponding 5,6-trans isomer in ca. 3:1 ratio) were extracted with ether, and the ether phase was washed as before. Compound 1c was purified by TLC (50% EtOAc in hexane, R_f 0.32) followed by high-pressure LC (6.4 × 250 mm column, 2.5% 2-propanol in hexane, at 2 mL/min and 900 psi). Product 1c, eluting at 63 mL, was recycled through the column and obtained in pure form in 20.2% yield from 6: UV λ_{max} 264 nm (ε, 18 000); mass spectrum, m/e 430 (M^+, 10), 370 (65), 269 (10), 134 (100); NMR δ 0.58 (s, 3 H, 18-CH_3), 0.99 (d, J = 5.9 Hz, 3 H, 21-CH_3), 2.03 (s, 3 H, 3-$OCOCH_3$), 3.66 (s, 3 H, 23-$COOCH_3$), 4.4 (m, 1 H, 1-H), 5.01 (s, 1 H, 19(*Z*)-H), 5.21 (m, 1 H, 3α-H), 5.34 (s, 1 H, 19(*E*)-H), 6.02 (d, J = 11.0 Hz, 1 H, 7-H), 6.34 (d, J = 11.0 Hz, 1 H, 6-H). Mild hydrolysis of 1c (75 μL of 0.1 M KOH/MeOH and 200 μL of ether, 15 °C, 60 min) provided 1b: UV λ_{max} 264 nm (ε, 18 000); high-resolution mass spectrum, calcd for $C_{24}H_{36}O_4$ 388.2614, found 388.2645; mass spectrum, m/e (relative intensity) 388 (18), 370 (61), 357 (3), 352 (24), 314 (1), 287 (1), 269 (4), 251 (7), 152 (31), 134 (100); NMR δ 0.58 (s, 3 H, 18-CH_3), 0.99 (d, J = 5.9 Hz, 3 H, 21-CH_3), 3.67 (s, 3 H, $COOCH_3$), 4.23 (m, 1 H, 3α-H), 4.43 (m, 1 H, 1β-H), 5.00 (s, 1 H, 19(*Z*)-H), 5.33 (s, 1 H, 19(*E*)-H), 6.02 (d, J = 11.0 Hz, 1 H, 7-H), 6.38 (d, J = 11.0 Hz, 1 H, 6-H). Hydrolysis of 1b in 10% KOH/90% methanol at 60 °C for 30 min followed by neutralization and filtration in 100% ethanol gives quantitative yields (by TLC and UV) of the natural product 1a.

Comparison with Biologically Generated 1b. The low-resolution mass spectrum and the UV spectrum for synthetic 1b were identical with the spectra obtained for the methylated metabolite isolated from 1,25-$(OH)_2D_3$-treated rats.[3] (Direct comparison of NMR spectra was not possible because the low quantities of isolated natural product[3] precluded NMR measurements.) For confirmation of chromatographic identity, [3α-^{3}H]calcitroic acid was obtained from the livers of rats dosed with [3α-^{3}H]-1α,25-dihydroxyD_3 and converted to its methyl ester (1b) as described by Esvelt et al.[3] This material (6500 dpm) was combined with 2 μg of synthetic 1b and the mixture was chromatographed on high-pressure LC using the 4.6 × 250 mm column eluted with 8% 2-propanol in hexane, and the absorbance was monitored at 254 nm. Fractions were collected, evaporated, and counted. Radioactivity coeluted exactly with the UV-absorbing peak due to synthetic 1b (elution volume, 40 mL).

Registry No. 1a, 71204-89-2; 1b, 71203-48-0; 1c, 75716-71-1; 1c 5,6-*trans* isomer, 75716-72-2; 2, 1474-14-2; 3, 33168-65-9; 4a, 75716-73-3; 4b, 75716-74-4; 5, 75716-75-5; 6, 75716-76-6; 6 3-tosyl derivative, 75731-72-5; 7, 75716-77-7; 8, 75731-73-6.

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1,3-Dithiane-2-carbodithioate: Synthesis and Reactivity Patterns

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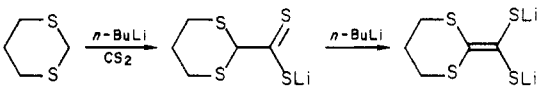
Received September 26, 1980

Introduction

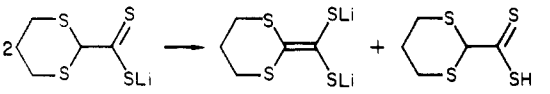
Work in these laboratories had centered on the design and syntheses of novel sulfur-containing molecules which promise to generate unique coordination chemistry with transition metals.[1] For the most part, this work has concentrated on new dithiolate and dithiocarbamate ligands. Our recent attempts to investigate the coordination chemistry of molecules containing the "tetrathiaethylene" unit have resulted in the syntheses of several new and interesting organosulfur species. In this note we report the syntheses and alkylation products of the 1,3-dithiane-2-carbodithioate dianion (2) and the corresponding monoanion (1).

Scheme I



1 2

Scheme II

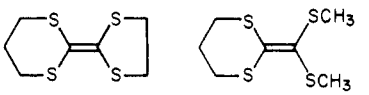


2 3

The chemistry of the 1,3-dithiane ring system is quite extensive. 1,3-Dithiane is probably best known as an acyl anion equivalent.[2] However, derivatives of 1,3-dithiane have also been of considerable interest in studies concerned with the conformational properties of heterocyclic molecules.[3] Ketene thioacetals have received considerable attention lately as useful organic intermediates.[4] The compounds reported here should be of interest in all of these areas. The most promising aspect of this work may be the ability to produce "asymmetric" molecules containing the tetrathiaethylene unit. Enormous interest in molecules containing this unit has been generated by the ability of this class of compounds to form charge-transfer complexes with TCNQ and some of its derivatives.[5] Until now, however, there has not been a facile method to prepare unsymmetrical tetrathiaethylene derivatives.

Discussion

Dilithio-1,3-dithiane-2-carbodithioate can be prepared from lithio-1,3-dithiane and CS_2 followed immediately by a second equivalent of *n*-BuLi as outlined in Scheme I. The second equivalent of *n*-BuLi must be added quickly since the C-2 proton of the monoanion 1 is extremely acidic due to its position α to two sulfides[6] as well as α to the dithiocarboxylate group. Failure to add *n*-BuLi results in a disproportionation reaction (Scheme II) to yield 2 and the extremely unstable dithioacid 3 which quickly decomposes. Dianion 2 is a white powder which can be alkylated without further isolation or it can be isolated and stored under argon at a temperature lower than −20 °C. Temperatures higher than −20 °C or contact with air instantly transform 2 into a smelly red oil of unknown composition. 2 can be alkylated with normal alkyl halides. For example, reaction of 2 with 1,2-dibromoethane yields 2-(1,3-dithiolan-2-ylidene)-1,3-dithiane (4) while reaction with 2 equiv of methyl iodide produces the dimethyl dithioacetal 5.



4 5

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