83948-57-6; **13b**, 83948-58-7; **14**, 83948-59-8; **15**, 83948-60-1; **16a**, 83948-61-2; **16b**, 83966-23-8; **18**, 83948-62-3; **19**, 83948-64-5; **21**, 83948-65-6; **23**, 144-16-1; **24**, 81505-61-5; **25**, 83948-66-7; **26**, 83948-67-8; **27a**, 83948-68-9; **27b**, 26163-65-5; **27**, 83966-24-9; **28a**, 83948-69-0; **28b**, 83948-70-3; **28c**, 83966-25-0; **29a**, 83948-71-4; **29b**, 83948-72-5; **29c**, 83948-73-6; **30a**, 83948-74-7; **31**, 83948-75-8; **32**, 83948-76-9; **33**, 83948-77-0; **34a**, 83948-78-1; **34b**, 83948-79-2; *O*-benzylhydroxylamine hydrochloride, 2687-43-6; benzyl chloroformate, 501-53-1; di-*tert*-butyl dicarbonate, 24424-99-5; *p*-nitrobenzyl chloroformate, 4457-32-3.

New Construction of a Steroidal Ring System. Stereoselective Synthesis of (±)-Androstane-2,17-dione

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Intramolecular Diels–Alder reaction of the triene **3** afforded the tricyclic olefin **4** which, after deprotection of the ketal groups, was treated with ethylaluminum dichloride to give (±)-androstane-2,17-dione (**6**) stereoselectively.

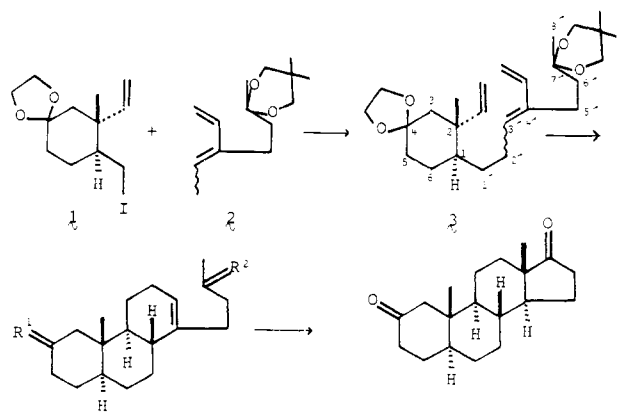
In a recent development toward the synthesis of steroids, the intramolecular cycloaddition reaction has played an important role because of its effective regio- and stereoselectivity. Among the numerous reports using it as a key step, much attention has been focused on the synthesis of A-aromatic steroids[1,2] such as estrone and estradiol and on the stereocontrolled construction of *trans*-hydrindan ring systems.[3] We now report a novel stereoselective synthesis of a nonaromatic steroid employing an intramolecular Diels–Alder reaction and a subsequent Lewis acid catalyzed ring-closure reaction as key steps.

Results and Discussion

For the purpose of accomplishment of our synthetic strategy, illustrated in Scheme I, the dienophile **1** was prepared from Hagemann's ester according to the method reported by us,[4] whereas the diene **2** was synthesized as follows (Scheme II).

Ethyl 2,5,5-trimethyl-1,3-dioxane-2-acetate (**7**),[5] on treatment with lithium aluminum hydride (3 equiv) in tetrahydrofuran at ambient temperature afforded the alcohol **8**, which was then converted to the iodide **10** via the tosylate **9** by tosylation of **8** with *p*-toluenesulfonyl chloride (1.5 equiv) and pyridine (2 equiv) in methylene chloride

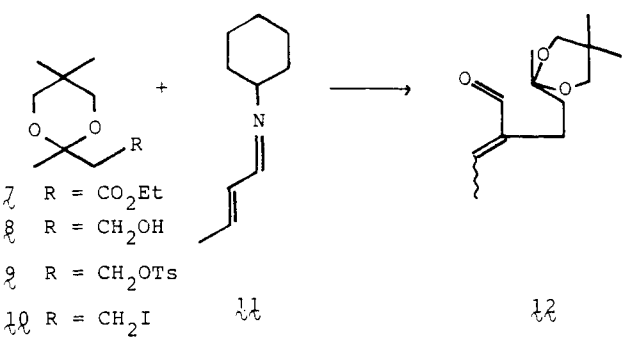
Scheme I



4 $R^1 = O(CH_2)_2O$, $R^2 = OCH_2C(CH_3)_2CH_2O$

5 $R^1 = R^2 = O$

Scheme II



7 R = CO_2Et

8 R = CH_2OH

9 R = CH_2OTs

10 R = CH_2I

and subsequent treatment of **9** with sodium iodide (5 equiv) in acetone (65% yield from **7**). Regioselective alkylation of crotonaldehyde with the iodide **10** has been carried out by using the Schiff base **11** and lithium diisopropylamide (1.1 equiv) under the conditions reported by Schlessinger[6] to afford the α-alkylated product **12** in 45% yield. Wittig methylenation[7] of **12** with triphenylmethylphosphonium bromide (2.5 equiv) and *n*-butyl-

(1) (a) Kametani, T.; Nemoto, H.; Ishikawa, H.; Shiroyama, K.; Fukumoto, K. *J. Am. Chem. Soc.* **1976**, *98*, 3378. (b) Kametani, T.; Nemoto, H.; Ishikawa, H.; Shiroyama, K.; Fukumoto, K. *Ibid.* **1977**, *99*, 3461. (c) Oppolzer, W.; Bättig, K.; Petrzilka, M. *Helv. Chim. Acta* **1978**, *61*, 1945. (d) Funk, R. L.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1977**, *99*, 5483; **1979**, *101*, 215; **1980**, *102*, 5253. (e) Djuric, S.; Sarker, T.; Magnus, P. *Ibid.* **1980**, *102*, 6885. (f) Grieco, P. A.; Takigawa, T.; Schillinger, W. J. *J. Org. Chem.* **1980**, *45*, 2247. (g) Nicolaou, K. C.; Barnette, W. E. *J. Chem. Soc., Chem. Commun.* **1979**, 1119. (h) Ito, Y.; Nakatsuka, M.; Saegusa, T. *J. Am. Chem. Soc.* **1981**, *103*, 476. (i) Tsuji, J.; Okumoto, H.; Kobayashi, Y.; Takahashi, T. *Tetrahedron Lett.* **1981**, *22*, 1357. (j) Quinkert, G.; Schwarts, U.; Stark, H.; Weber, W. D.; Baier, H.; Adam, F.; Durner, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 1029. (k) For a recent review, see: Oppolzer, W. *Synthesis* **1978**, 793. (l) Nicolaou, K. C.; Barnette, W. E.; Ma, P. *J. Org. Chem.* **1980**, *45*, 1463. (k) Oppolzer, W.; Roberts, D. A.; Bird, T. G. C. *Helv. Chim. Acta* **1979**, *62*, 2017. (n) Kametani, T.; Nemoto, H. *Tetrahedron* **1981**, *37*, 3.

(2) Recently Stork has published an impressive paper on the synthesis of an 11-oxygenated steroid by an intramolecular Diels–Alder reaction. See: Stork, G.; Clark, G.; Shiner, C. S. *J. Am. Chem. Soc.* **1981**, *103*, 4948.

(3) (a) Jung, M. E.; Halweg, K. *Tetrahedron Lett.* **1981**, *22*, 3929. (b) Bal, S.; Helquist, P. *Ibid.* **1981**, *22*, 3933. (c) Roush, W.; Reseckis, S. *J. Am. Chem. Soc.* **1981**, *103*, 6696. (d) Kametani, T.; Matsumoto, H.; Honda, T.; Fukumoto, K. *Tetrahedron Lett.* **1980**, *21*, 4847.

(4) Kametani, T.; Tsubuki, M.; Nemoto, H. *J. Org. Chem.* **1980**, *45*, 4391.

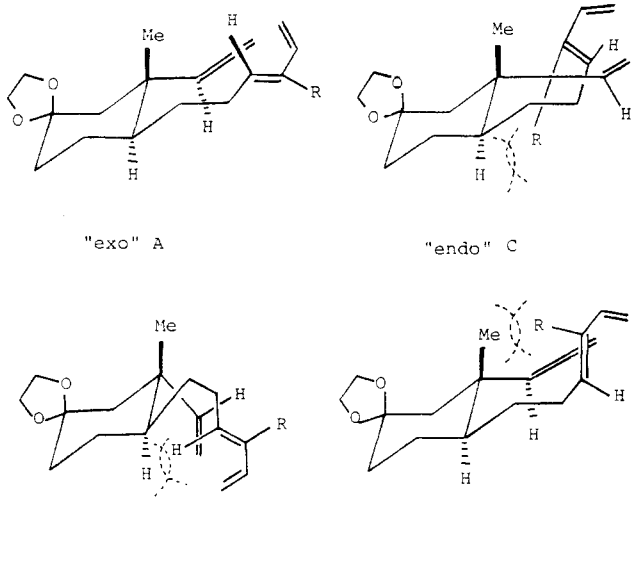
(5) Bruice, T. C.; Piszkiewicz, D. *J. Am. Chem. Soc.* **1967**, *89*, 3568.

(6) Kiecyzykowski, G. R.; Schlessinger, R. H.; Sulsky, R. B. *Tetrahedron Lett.* **1976**, 597 and references cited therein.

(7) Wittig, G.; Schoellkopf, U. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. 5, p 751.

0022-3263/83/1948-0031$01.50/0

Chart I



lithium (2.5 equiv) in tetrahydrofuran at ambient temperature gave rise to the diene **2** in 86% yield. Since it has been known[8] that an intramolecular Diels–Alder reaction is superior to that of an intermolecular one in terms of regio- and stereoselectivity, we next turned our attention to the coupling reaction of the diene **2** and the dienophile **1**. The pentadienyl anion, generated from **2** with *n*-butyllithium (1.1 equiv) in tetrahydrofuran and hexamethylphosphoric triamide (10:1 v/v) at −78 °C, was treated with the iodide **1** (1.0 equiv) at −78 °C for 3 h to give mixtures of *E* and *Z* double bond isomers **3** in 34% yield.[9,10] At the moment, the mixtures cannot be separated; however, both dienes would be expected to undergo an intramolecular Diels–Alder reaction.[11] Thus, a toluene solution of the triene **3** (5% w/v in a sealed tube) was heated at 200 °C for 3 h to yield the tricyclic compound **4** [mp 136–137 °C (from benzene/*n*-hexane)] as a sole cyclized product[12] in 62% yield. This stereoselectivity[13] can be rationalized by assuming that the cycloaddition reaction would proceed through the sterically favored exo transition state (A) leading to **4**, rather than through the other three possible transition states (B–D) as shown in Chart I. The second exo transition state (B), which would lead to an isomer of **4** having a trans–syn–trans configuration of the hydrophenanthrene ring system, suffers from an interaction between C_1–H and C_3–H. Of the two diastereomeric endo transition states (C and D), C is clearly the worst in terms of a nonbonded interaction between C_1H and the alkyl substituent (R). The second endo transition state (D) suffers from an interaction between the angular methyl group and the alkyl substituent at the 4′-position of **3**.

Since we succeeded in the stereoselective synthesis of the A–C ring systems of the steroid, we next investigated a Lewis acid catalyzed cyclization reaction, which would control a C/D ring juncture to be trans and would introduce a C_{18} methyl group simultaneously.[14] The olefin **4** was treated with a catalytic amount of *p*-toluenesulfonic acid in acetone at ambient temperature for 1 h[15] to give rise to the diketone **5** [mp 105–106 °C (from benzene/*n*-hexane)] in quantitative yield. Among the several attempts for the conversion of **5** into **6**, a moderate yield was obtained by treatment of **5** with ethylaluminum dichloride (3 equiv) in methylene chloride at 0 °C for 6 h (31% yield), and the synthetic (±)-androstane-2,17-dione [mp 175.5–177.5 °C (from benzene/*n*-hexane)] was identical with an authentic specimen[16] donated by Prof. Kirk, except for the melting point and optical rotation.

Thus, the facile and stereocontrolled synthesis of (±)-androstane-2,17-dione has been achieved by an intramolecular cycloaddition reaction and a subsequent ring-closure reaction catalyzed with Lewis acid as key steps, and this type of synthesis would provide a possibility for the synthesis of a wide variety of functionalized nonaromatic steroids.

Experimental Section

Infrared spectra were run on a Hitachi 260-10 spectrophotometer in $CHCl_3$ solution. NMR spectra were determined with JEOL JNM-FX-100 spectrometer in $CDCl_3$ or CCl_4 solutions, and chemical shifts are expressed in parts per million downfield from internal tetramethylsilane. Mass spectra were obtained with a JEOL JMS-D300 spectrometer.

2-(2-Hydroxyethyl)-2,5,5-trimethyl-1,3-dioxane (8). To a stirred suspension of $LiAlH_4$ (2.85 g, 75.1 mmol) in THF (100 mL) was added a solution of the ester **7** (21.6 g, 100 mmol) in THF (100 mL) at 0 °C, and the resulting mixture was stirred at room temperature for 12 h. To the above mixture was added Et_2O (300 mL) and 15% NaOH solution (10 mL) at 0 °C. The insoluble materials were removed by filtration, and the filtrate was washed with brine, dried over Na_2SO_4, and evaporated to give the alcohol **8** (14.9 g, 85%) as a colorless oil, which was used in the next reaction without further purification: ^{1}H NMR (CCl_4) δ 0.81 (3 H, s, CH_3), 1.07 (3 H, s, CH_3), 1.35 (3 H, s, CH_3), 1.82 (2 H, t, J = 6 Hz, CH_2CH_2OH), 3.33 (2 H, d, J = 12 Hz, $OCH_2C(CH_3)_2$), 3.58 (2 H, d, J = 12 Hz, $OCH_2C(CH_3)_2$), 3.73 (2 H, t, J = 6 Hz, CH_2CH_2OH).

2-[2-(*p*-Toluenesulfonyloxy)ethyl]-2,5,5-trimethyl-1,3-dioxane (9). A solution of the alcohol **8** (2 g, 11.5 mmol), pyridine (1.8 g, 22.8 mmol), and *p*-TsCl (3.3 g, 17.3 mmol) in CH_2Cl_2 (50 mL) was stirred for 24 h at ambient temperature. The resulting mixture was then washed with H_2O, dried over Na_2SO_4, and evaporated. The residue was rapidly purified by column chromatography on silica gel to afford the tosylate **9** (3.5 g, 92.8%) as a colorless oil with benzene as the eluant. This compound was used immediately in the next reaction because of its instability: ^{1}H NMR ($CDCl_3$) δ 0.78 (3 H, s, CH_3), 0.90 (3 H, s, CH_3), 1.29 (3 H, s, CH_3), 2.03 (2 H, t, J = 7.5 Hz, CH_2CH_2OTs), 2.70 (3 H, s, $ArCH_3$), 3.25 (2 H, d, J = 11.5 Hz, $OCH_2C(CH_3)_2$), 3.46 (2 H, d, J = 11.5 Hz, $OCH_2C(CH_3)_2$), 4.19 (2 H, t, J = 7.5 Hz, CH_2OTs), 7.23 (2 H, d, J = 9 Hz, 2 Ar H), 7.71 (2 H, d, J = 9 Hz, 2 Ar H); MS, m/e 313 (M^+ − 15).

2-(2-Iodoethyl)-2,5,5-trimethyl-1,3-dioxane (10). A mixture of the tosylate **9** (2 g, 6.1 mmol), NaI (4.6 g, 30.7 mmol), and acetone (50 mL) was stirred for 2 days at room temperature. After

(8) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 10 and references cited therein.

(9) Wilson, S. R.; Misra, R. N. *J. Org. Chem.* **1980**, *45*, 5079. 3-Substituted 1,4-pentadiene was used to generate a 1,4-pentadienyl anion.

(10) The ratio of *E*/*Z* for **3** could not be determined at this stage.

(11) (a) Boeckman, R. K., Jr.; Alessi, T. R. *J. Am. Chem. Soc.* **1982**, *104*, 3216. (b) Pyne, S. G.; Hensel, M. J.; Byrn, S. R.; Mckenzie, A. T.; Fuchs, P. L. *Ibid.* **1980**, *102*, 5960. (c) House, H. O.; Cronin, T. H. *J. Org. Chem.* **1965**, *30*, 1061.

(12) The noncyclized products, which are mainly decomposed compounds, are easily separated from **4** by crystallization. The 1,5-hydrogen-shifted product and any other possible regio- and stereoisomers could not be isolated.

(13) Though the stereochemistry for **4** remains ambiguous at the moment, it was concluded to be **4** by its conversion into **6**.

(14) This work has been originally investigated by Snider, who published the synthesis of a *trans*-hydrindanone: Karras, M.; Snider, B. B. *J. Am. Chem. Soc.* **1980**, *102*, 7951.

(15) We have found that the shorter reaction time brought about the selective monodeketalization; however, this selectivity is lacking in reproducibility.

(16) (a) Djerassi, C.; Yashin, R.; Rosenkranz, G. *J. Am. Chem. Soc.* **1950**, *72*, 5750. (b) Clark, R. L. *J. Org. Chem.* **1963**, *28*, 2626. (c) Bridgeman, J. E.; Butchers, C. E.; Jones, E. R. H.; Kasal, A.; Meakins, G. D.; Woodgate, P. D. *J. Chem. Soc. C* **1970**, 244.

evaporation of the solvent, the residue was extracted with AcOEt, and the extract was washed with aqueous $Na_2S_2O_3$ solution, dried over Na_2SO_4, and evaporated to give the residue, which was purified by column chromatography on silica gel with benzene as the eluant to afford the iodide **10** (1.35 g, 81.6%) as a yellowish oil which was immediately used in the next reaction: ^1H NMR ($CDCl_3$) δ 0.83 (3 H, s, CH_3), 1.03 (3 H, s, CH_3), 1.31 (3 H, s, CH_3), 2.04–2.41 (2 H, m, CH_2CH_2I), 3.03–3.43 (2 H, m, CH_2I), 3.26 (2 H, d, J = 11.5 Hz, $OCH_2C(CH_3)_2$), 3.51 (2 H, d, J = 11.5 Hz, $OCH_2C(CH_3)_2$); MS, m/e 269 (M^+ – 15).

2-(3-Formyl-3-pentenyl)-2,5,5-trimethyl-1,3-dioxane (12). To a stirred solution of LDA (353 mg, 3.3 mmol) in THF–HMPA (5 and 0.56 mL, respectively) was added a solution of **11** (453 mg, 3 mmol) in THF (5 mL) at –78 °C. After the mixture was stirred for 30 min at the same temperature under a current of nitrogen, a solution of the iodide **10** (937 mg, 3.3 mmol) in THF (10 mL) was added to the above solution, and the resulting mixture was further stirred for 3 h at –78 °C. Et_2O (100 mL) and aqueous NH_4Cl solution were added, and the mixture was stirred for 30 min at ambient temperature. The organic layer was separated, washed with brine, dried over Na_2SO_4, and evaporated to give the residue, which was subjected to column chromatography on silica gel. Elution with benzene afforded the aldehyde **12**: 300 mg (44.2%); yellow oil; IR ($CHCl_3$) ν_{max} 1675 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.93 (3 H, s, CH_3), 0.99 (3 H, s, CH_3), 1.38 (3 H, s, CH_3), 2.06 (3 H, d, J = 7 Hz, C=$CHCH_3$), 3.48 (4 H, s, 2 $OCH_2C(CH_3)_2$), 6.54 (1 H, q, J = 7 Hz, C=$CHCH_3$), 9.29 (1 H, s, CHO). Anal. Calcd $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 68.49; H, 10.03.

2,5,5-Trimethyl-2-(3-ethenyl-3-pentenyl)-1,3-dioxane (2). To a stirred suspension of methyltriphenylphosphonium bromide (1.8 g, 5 mmol) in THF (30 mL) was added a solution of *n*-BuLi (320 mg, 5 mmol) in hexane (3.2 mL) under a current of nitrogen at 0 °C. After the mixture was stirred for 15 min at 0 °C, a solution of the aldehyde **12** (450 mg, 2 mmol) in THF (4 mL) was added to the above solution. After being stirred for 4 h at 0 °C, the resulting mixture was diluted with Et_2O (300 mL), washed with brine, dried over Na_2SO_4, and evaporated to give the residue, which was chromatographed on silica gel with benzene as the eluant to afford the diene **2**: 380 mg (85.2%); colorless oil; IR ($CHCl_3$) ν_{max} 1635 cm^{-1}; ^1H NMR (CCl_4) δ 0.81 (3 H, s, CH_3), 1.01 (3 H, s, CH_3), 1.28 (3 H, s, CH_3), 1.68 (3 H, d, J = 6.5 Hz, >C=$CHCH_3$), 3.30 (2 H, d, J = 11 Hz, $OCH_2C(CH_3)_2$), 3.36 (2 H, d, J = 11 Hz, $OCH_2C(CH_3)_2$), 4.78 (1 H, d, J = 10.5 Hz, *trans*-HC=CH**H**), 5.03 (1 H, d, J = 18 Hz, *cis*-HC=CH**H**), 5.40 (1 H, q, J = 6.5 Hz, >C=C**H**CH_3), 6.10 (1 H, dd, J = 10.5, 18 Hz, C**H**=CH_2); MS, m/e 224 (M^+). Anal. Calcd $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 75.07; H, 10.75.

2α-Ethenyl-1β-[4-ethenyl-7,7-(2,2-dimethyl-1,3-propylenedioxy)-3-octenyl]-4,4-(1,2-ethylenedioxy)-2β-methylcyclohexane (3). To a stirred solution of the diene **2** (300 mg, 1.34 mmol) in THF–HMPA (8 and 0.8 mL, respectively) was added a solution of *n*-BuLi (95 mg, 1.34 mmol) in hexane (0.95 mL) at –78 °C. After the mixture was stirred for 30 min at –78 °C, a solution of the iodide **1** (430 mg, 1.34 mmol) in THF (5 mL) was added to the above solution, and the resulting mixture was further stirred for 3 h at –78 °C. The reaction mixture was extracted with Et_2O (100 mL), and the extract was washed with aqueous $Na_2S_2O_3$ solution, dried over Na_2SO_4, and evaporated to give the residue, which was subjected to column chromatography on silica gel. Elution with benzene–AcOEt (20:1) afforded the triene **3**: 170 mg (33.9%); colorless oil; IR ($CHCl_3$) ν_{max} 1635 cm^{-1}; ^1H NMR (CCl_4) δ 0.83 (3 H, s, CH_3), 0.97 (3 H, s, CH_3), 1.03 (3 H, s, CH_3), 1.31 (3 H, s, CH_3), 3.40 (2 H, d, J = 11 Hz, $OCH_2C(CH_3)_2$), 3.50 (2 H, d, J = 11 Hz, $OCH_2C(CH_3)_2$), 3.83 (4 H, s, OCH_2CH_2O), 4.70–6.45 (7 H, m, olefinic protons).

1-[3,3-(2,2-Dimethyl-1,3-propylenedioxy)butyl]-6,6-(1,2-ethylenedioxy)-4bβ-methyl-3,4,4aα,5,6,7,8,8aα,9,10,10aβ-undecahydrophenanthrene (4). A solution of the triene **3** (250 mg, 0.6 mmol) in toluene (5 mL) was heated for 2 h at 180–200 °C in a sealed tube. After the solvent had been removed, the residue was subjected to the column chromatography on silica gel. Elution with benzene gave the compound **4**: 150 mg (60%); colorless needles; mp 136–137 °C (from hexane); ^1H NMR ($CDCl_3$) δ 0.87 (3 H, s, CH_3), 0.90 (3 H, s, CH_3), 1.00 (3 H, s, CH_3), 1.36 (3 H, s, CH_3), 3.46 (2 H, d, J = 6 Hz, $OCH_2C(CH_3)_2$), 3.51 (2 H, d, J = 6 Hz, $OCH_2C(CH_3)_2$), 3.76–4.06 (4 H, m, OCH_2CH_2O), 5.38 (1 H, br s, C=CH). Anal. Calcd $C_{26}H_{42}O_4$: C, 74.60; H, 10.11. Found: C, 74.23; H, 10.31.

4bβ-Methyl-1-(3-oxobutyl)-3,4,4aα,5,6,7,8,8aα,9,10,10aβ-undecahydrophenanthren-6-one (5). A solution of **4** (44 mg, 0.105 mmol) and a catalytic amount of *p*-TsOH in acetone (10 mL) was stirred for 1 h at ambient temperature. The reaction mixture was extracted with AcOEt (100 mL), and the extract was washed with aqueous $NaHCO_3$ solution, dried over Na_2SO_4, and evaporated to give the residue, which was crystallized from benzene–hexane to afford the diketone **5**: 27 mg (90%); mp 105–106 °C (from benzene–hexane); colorless needles; IR ($CHCl_3$) ν_{max} 1715 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.69 (3 H, s, CH_3), 2.05 (3 H, s, CH_3), 5.25 (1 H, br s, C=CH); MS, calcd for $C_{19}H_{28}O_2$ m/e 288.2088 (M^+), found m/e 288.2050 (M^+).

(±)-5α-Androstane-2,17-dione (6). To a stirred solution of the diketone **5** (71 mg, 0.246 mmol) in CH_2Cl_2 (5 mL) was added a solution of $EtAlCl_2$ (94 mg, 0.74 mmol) in toluene (0.5 mL) under a current of nitrogen at 0 °C. After the mixture was stirred for 6 h at 0 °C, aqueous $NaHCO_3$ solution was added and the mixture extracted with CH_2Cl_2. The extract was washed with brine, dried over Na_2SO_4, and evaporated to give the residue, which was subjected to column chromatography on silica gel. Elution with benzene–AcOEt (10:1) gave a colorless oil, which was crystallized from benzene–hexane to afford the title compound (**6**): 22 mg (31%); colorless needles; mp 175.5–177.5 °C; IR ($CHCl_3$) ν_{max} 1740, 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.77 (3 H, d, J = 0.8 Hz, CH_3), 0.85 (3 H, s, CH_3). All the spectral data, except the melting point and optical rotation, of **6** were identical with those of an authentic sample donated by Prof. Kirk.

Acknowledgment. We are grateful to Prof. D. N. Kirk, Steroid Reference Collection, Chemistry Department, Westfield College, Hampstead, London, for a generous gift of androstane-2,17-dione. We also thank Prof. Sir Ewart Jones, who donated the above sample to the Medicinal Research Council. Thanks are also due to Mrs. T. Ogata, Miss M. Shigetsuna, Miss M. Nagao, Mrs. A. Kumazawa, and Miss Y. Narita, Faculty of Pharmaceutical Sciences, Hoshi University, for microanalyses, spectral measurements, and preparation of the manuscript.

Registry No. (±)-**1**, 83916-56-7; **2**, 83862-39-9; (±)-(*E*)-**3**, 83862-40-2; (±)-(*Z*)-**3**, 83916-57-8; (±)-**4**, 83862-41-3; (±)-**5**, 83862-42-4; (±)-**6**, 83862-43-5; **7**, 5406-47-3; **8**, 83862-44-6; **9**, 83862-45-7; **10**, 83862-46-8; **11**, 1197-53-1; **12**, 83862-47-9; methyltriphenylphosphonium bromide, 1779-49-3.