Cholestenone. The literature method[7] was modified by using aluminum isopropoxide in place of aluminum *tert*-butoxide. A solution of 21 g of freshly distilled aluminum isopropoxide in 130 mL of benzene was added to a solution of 30 g of cholesterol in 350 mL of benzene and 250 mL of acetone. After the mixture was refluxed for 48 h, the product was isolated as described[7] to give 18 g of cholestenone, mp 80–81.5 °C (lit.[7] mp 78.5–80.5 °C). The filtrate was subjected to recycling which raised the overall yield to 85–90%.

24-Hydroxychol-4-en-3-one Acetate (I). Cholestenone (0.50 g) was dissolved at 0 °C in a solution of 19.5 mL of CF_3COOH, 10.5 mL of 96% H_2SO_4, and 1.0 mL of 50% aqueous H_2O_2. After being stirred for 4 h at 0 °C, the solution was quenched by slow addition to ice–water. A hexane extract was washed with 5% $NaHCO_3$ and dried over $MgSO_4$.

After removal of solvent in vacuo at 25 °C, the residue was dissolved in a solution of 50 mL of acetic acid, 2 mL of water, and 1.0 g of sodium acetate. The solution was refluxed for 18 h under N_2, cooled, and diluted with 100 mL of water. A hexane extract was washed with 5% Na_2CO_3 and dried over $MgSO_4$. Removal of solvent in vacuo at 25 °C gave 0.15 g of crystalline acetate (I). A GC analysis indicated that it was 70% pure with the remainder being unreacted cholestenone.

The impure I was chromatographed on 10 g of 28–200 mesh silica gel, using 65:35 hexane–ether. Cholestenone eluted before I. The purified I was recrystallized from methanol to give 0.087 g (17%) of white needles: mp 123–125 °C; NMR ($CDCl_3$) δ 0.68 (s, 3 H, CH_3 at C-18), 1.13 (s, 3 H, CH_3 at C-19), 2.03 (s, 3 H, acetate), 4.02 (m, 2 H, C-24 CH_2Oac), 5.67 (s, 1 H, vinyl H at C-4); IR (KBr) 1735 (s), 1675 (s), 1242 (s), 1030 (m); exact mass calcd for $C_{26}H_{40}O_3$ *m/e* 400.2976, found 400.2996.

24-Hydroxychol-4-en-3-one. A mixture of 0.089 g of I, 10 mL of 95% ethanol, and 0.60 g of KOH was stirred for 2 h at 25 °C under N_2 followed by addition to water. The ether extract was dried over $MgSO_4$ and the ether removed at 25 °C. Recrystallization from acetone gave 0.070 g (89%) of white needles of 24-hydroxychol-4-en-3-one, mp 131.5–133.5 °C (lit.[8] 131–132 °C).

Competition Reactions. A typical study involved addition of 2.2 mmol of isooctane and 2.2 mmol of the α,β-unsaturated ketone to a solution of 25 mL of CF_3COOH, 4 mL of 96% H_2SO_4, and 1.0 mL of 50% aqueous H_2O_2 at 0 °C. The progress of the reaction was monitored at 25 °C by NMR.

Acknowledgment. This work was supported by the Pennsylvania Research Corporation and by the National Institute of Health. The assistance of Dr. Robert D. Minard is also acknowledged in connection with all mass spectra measurements.

Registry No. I, 74854-66-3; cholesterol, 57-88-5; cholestenone, 601-57-0; 24-hydroxychol-4-en-3-one, 17597-30-7.

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Synthesis of Deoxyhalogeno Sugars. Displacement of the (Trifluoromethanesulfonyl)oxy (Triflyl) Group by Halide Ion[1]

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A new method for synthesis of deoxyhalogeno sugars is described. This reaction sequence consists of esterifying partially protected carbohydrates with trifluoromethanesulfonic (triflic) anhydride and reacting the resulting trifluoromethanesulfonates with tetrabutylammonium halides. This process for formation of halogenated carbohydrates is mild and convenient. It does not experience the difficulties, such as molecular rearrangement and lack of reactivity at secondary carbons, which sometimes are encountered in displacement reactions in carbohydrate systems.

Deoxyhalogeno sugars are among the most important and useful compounds in carbohydrate chemistry. They assume key roles in the syntheses of aminodeoxy, deoxy, and anhydro sugars; also, they serve as synthetic intermediates in the introduction of heteroatoms and unsaturation into carbohydrates and related structures. In addition to their synthetic importance, certain halogenated carbohydrates and nucleosides have biologically significant properties.[2]

The variety of functions for deoxyhalogeno sugars naturally has stimulated considerable interest in their syn-

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(1) A portion of this research has been published in preliminary form: Binkley, R. W.; Hehemann, D. G. *J. Org. Chem.* **1978**, *43*, 3244.

(2) A number of excellent reviews of the chemistry and biochemistry of deoxyhalogeno sugars have been published. These include: (a) Szarek, W. A. *Adv. Carbohydr. Biochem.* **1973**, *28*, 225; (b) Barnett, J. E. G. *Adv. Carbohydr. Chem.* **1967**, *22*, 177; (c) Hanessian, S. Adv. *Chem. Ser.* **1968**, *74*, 159; (d) Haines, A. H. *Adv. Carbohydr. Biochem.* **1976**, *33*, 72.

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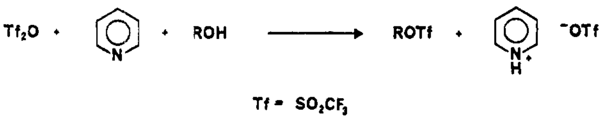
thesis. Although several types of reaction have been useful in obtaining halogenated carbohydrates, displacement processes generally have been most effective.[2] Many displacement reactions suffer, however, from one or more of the following limitations: (a) destructively vigorous reaction conditions, (b) inability to effect displacement in certain situations, particularly when the leaving group is attached to a secondary carbon, (c) competing elimination reactions, and (d) molecular rearrangements.

A reaction which overcomes many of these limiting factors is the displacement of the (trifluoromethanesulfonyl)oxy (triflyl) group with tetrabutylammonium halides. The effectiveness of this reaction can be attributed to a combination of two factors, the unusual ease of displacement of the triflyl group and the enhanced nucleophilicity of the halide ion in the form of its tetrabutylammonium salt. This combination permits facile introduction of halogens at both primary and secondary positions.

Results and Discussion

The general procedure for triflate synthesis consisted of reacting a dichloromethane solution of each partially protected carbohydrate (1–8) (Table I) with triflic anhydride in the presence of pyridine (eq 1). Complete esterification occurred for compounds 1–6 to produce the corresponding triflates 9–4 (Table I). The triflates 15 and 16 were too unstable to be isolated. The typical procedure was to minimize possible decomposition by reacting the triflates immediately after formation.



(1)

The spectral information which could be obtained from compounds 9–14 (Tables II and III) supported the structures assigned; however, the amount of information gathered depended upon the stability of each triflate. Both ^{1}H NMR and mass spectra were obtained for compounds 9–11. For 12–14 only ^{1}H NMR spectra were possible because thermal instability prevented mass spectral analysis. Due to thermal decomposition at room temperature, no spectral evidence could be obtained for the triflates 15 and 16. For each of the triflates 9–14 the assignment of structure was confirmed by conversion to the corresponding deoxyiodo sugars; for 15 and 16 the mode of triflate formation and conversion to known deoxyiodo sugars constituted the evidence for their existence.

The triflates 9–14 were converted into the corresponding iodides by refluxing in benzene in the presence of tetrabutylammonium iodide. (The percent yields and times required for reaction are given in Table IV.) Structures were assigned to the iodides 17–24 on the basis of their ^{1}H NMR (Table II) and mass spectra (Table III). These identifications were confirmed in each instance either by comparison with an independently synthesized sample of the iodide or in those cases where the iodide had not been reported previously, by conversion of the iodide to the known deoxy sugar.

Since the triflates 15 and 16 were unstable under the reaction conditions, alternatives to the normal procedure for their formation and reaction were explored. The work of Perlin[21] and Schuerch[22] suggested a possible approach, one which consisted of forming the triflate at −78 °C in the presence of tetrabutylammonium iodide and allowing reaction to occur as the mixture warmed to 25 °C. This procedure proved to be quite acceptable for formation of the iodides 23 and 24 (Table IV). A second alternative was

Table I

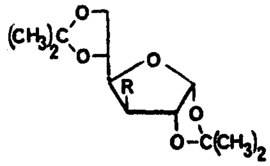
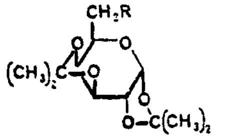
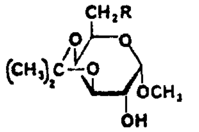
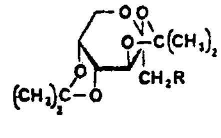
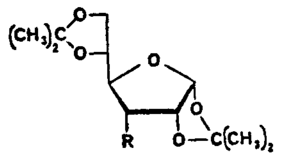
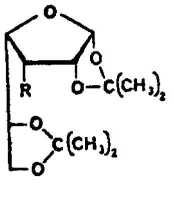
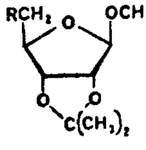
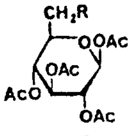
	R = OH	ref to source	R = OSO_2CF_3	ref to previous synthesis
	1	3	9	11
	2	4	10	11
	3	5	11	none
	4	6	12	none
	5	7	13	11
	6	8	14	none
	7	9	15	none
	8	10	16	none

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Table II.[a] ^{1}H NMR Spectral Data for Triflates 9–14 and Halides 17–31

compd	chemical shift values, δ							
	H-1	H-2	H-3	H-4	H-5	H-6	H-6′	misc
9	6.07 (d, J = 4.0 Hz)	4.82 (d, J = 4.0 Hz)	5.33 (br s)	4.37 —	—	—	— 3.87	1.50, 1.42 (CH_3's) 1.33 (2 CH_3)
10	5.53 (d, J = 5.0 Hz)	4.80–4.47	4.47 —	—	—	—	— 3.60	1.50, 1.42 (CH_3's) 1.32 (2 CH_3)
11	4.88 —	—	—	—	—	—	— 3.77	3.47 (s, CH_3), 3.07 (s, 2-OH), 1.47, 1.32 (OH_3's)
12	4.50 (br s)	4.88 —	—	—	—	—	— 3.53	1.56, 1.47, 1.40, 1.35 (CH_3's)
13	5.83 (d, J = 3.5 Hz)	5.10–4.65	4.33 —	—	—	—	— 3.67	1.55, 1.40, 1.35, 1.30 (CH_3's)
14	5.92 (d, J = 4.0 Hz)	5.48 —	—	—	—	—	— 3.36	1.60, 1.38 (CH_3's), 1.41 (2 CH_3)
17	5.77 (d, J = 3.8 Hz)	4.55 (t, J = 3.8 Hz)	4.40 —	—	—	—	— 3.52	1.53, 1.47 (CH_3's), 1.33 (2 CH_3)
18	5.38 (d, J = 5.0 Hz)	4.65 —	—	—	—	—	— 2.98	1.48, 1.38 (CH_3's), 1.30 (2 CH_3)
19	4.75 (d, J = 4.0 Hz)	4.50 —	—	—	—	—	— 3.17	3.50 (s, OCH_3), 2.70 (s, 2-OH), 1.47, 1.33 (CH_3's)
20	4.75 —	—	—	—	—	—	— 3.62	1.55, 1.48, 1.43, 1.35 (CH_3's)
21	5.95 (d, J = 3.5 Hz)	5.03 (d, J = 3.5 Hz)	4.47 (d, J = 3.0 Hz)	3.43–4.80	4.20 —	—	— 3.87	1.47, 1.37, 1.30, 1.27 (CH_3's)
22	5.92 (d, J = 4.3 Hz)	4.98 (d, J = 0.8, 4.3 Hz)	4.48 —	—	—	—	— 3.52	1.58, 1.43 (CH_3's), 1.37 (2 CH_3)
23	5.07 (s)	4.92 —	—	— 4.25	3.18 (m)			3.38 (OCH_3), 1.50, 1.32 (CH_3's)
24	5.92 —	—	—	— 4.77	3.82 —	—	— 2.92	2.10, 2.03 (CH_3's), 2.00 (2 CH_3)
25	5.01 (s)	4.82 —	—	—	—	—	— 4.25	3.37 (s, OCH_3), 1.47, 1.32 (CH_3's), 3.90 (J = 9.0 Hz, $CF_3CH_2SO_3^-$)
26	5.85 (d, J = 3.8 Hz)	4.75 (d, J = 3.8 Hz)	4.52 —	—	—	—	— 3.72	1.57, 1.47 (CH_3's), 1.37 (2 CH_3)
27	5.48 (d, J = 3.5 Hz)	4.73 (d, J = 3.5 Hz)	4.27 —	—	—	—	— 3.97	1.57, 1.47 (CH_3's), 1.37 (2 CH_3)
28	5.53 (d, J = 5.2 Hz)	4.38 (dd, J = 5.2, 1.2 Hz)	4.65 (dd, J = 8.0, 1.2 Hz)	4.35 —	—	—	— 3.28	1.55, 1.45 (CH_3's), 1.35 (2 CH_3)
29	5.50 (d, J = 5.1 Hz)	4.30 (dd, J = 5, 1 Hz)	4.63 (dd, J = 8.0, 1.0 Hz)	4.47 —	—	—	— 3.43	1.53, 1.43 (CH_3's), 1.33 (2 CH_3)
30	5.95 (d, J = 3.5 Hz)	4.88 (d, J = 3.5 Hz)	4.50 —	—	—	—	— 3.83	1.53, 1.42, 1.33, 1.30 (CH_3's)
31	5.92 (d, J = 3.0 Hz)	4.72 (t, J = 3.0 Hz)	4.20 —	—	—	—	— 3.80	1.50, 1.42, 1.33, 1.30 (CH_3's)

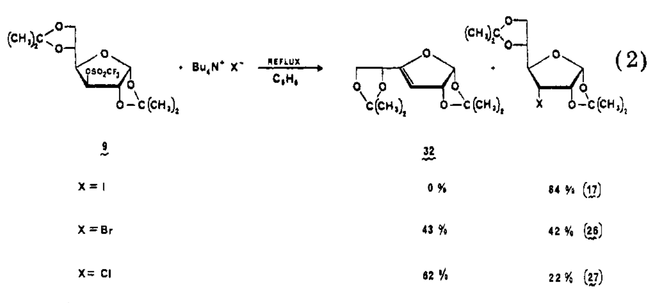
[a] s = singlet, d = doublet, t = triplet, m = multiplet.

Table III. Selected Peaks from the Electron-Impact Mass Spectra of Compounds 9–11, 17–23, and 26–31

compd	*m/e* (relative abundances)	
	M − 15	other significant ions
9	378 (2.51)	377 (17.08), 319 (7.53), 101 (100.00)
10	378 (2.50)	377 (15.54), 236 (47.77), 199 (100.00)
11	351 (30.10)	335 (7.14), 305 (8.67), 279 (20.92)
17	355 (100.00)	297 (9.46), 269 (22.27), 255 (6.27)
18	355 (100.00)	370 (10.41), 356 (12.50), 297 (6.25)
19	329 (15.09)	254 (22.26), 225 (16.60), 209 (8.30)
20	355 (33.84)	356 (3.81), 297 (4.32), 255 (2.29)
21	355 (34.64)	297 (16.46), 295 (3.44)
22	355 (6.21)	110 (8.58), 101 (100.00)
23	299 (10.27)	128 (8.98), 127 (100.00)
26	309 (8.43) 307 (8.03)	163 (6.02), 101 (100.00)
27	265 (6.98) 263 (21.66)	177 (5.26), 147 (6.85), 145 (16.03)
28	309 (33.05) 307 (33.72)	171 (8.22), 189 (8.89)
29	265 (27.72) 263 (78.61)	221 (6.43), 147 (9.16), 145 (26.68)
30	309 (2.27) 307 (2.65)	251 (3.14), 249 (3.47)
31	265 (8.46) 263 (24.48)	207 (5.94), 205 (18.70)

to replace the triflyl group with the less reactive (2,2,2-trifluoroethanesulfonyl)oxy (tresyl) group. The tresylate **25** formed readily, did not decompose during isolation, and reacted with tetrabutylammonium iodide to give **23** in excellent yield (Table IV); however, the difficulty in synthesis of the tresyl chloride (necessary for obtaining **25**) made tresylate formation a relatively unattractive pathway.

Displacement by chloride and bromide ions was investigated on three compounds, a primary triflate (**10**), a secondary triflate (**13**), and a secondary triflate (**9**) for which substitution is known to be difficult. (Product identities and yields are given in Table IV.) Displacement occurred readily on **10** and **13** but, unlike reaction with iodide, displacements on the hindered triflate **9** using the more basic bromide and chloride ions resulted in elimination competing with substitution (eq 2). During these



reactions it was necessary to add sodium bicarbonate to the reaction mixtures in which elimination was taking place; otherwise, the acid liberated caused complete product decomposition. (Flechtner recently has shown that quantitative elimination occurs when the triflate **9** is treated with strong bases.[23])

In conclusion, the results described here show that triflate displacement is a convenient and mild method for formation of deoxyhalogeno sugars. Triflate formation and

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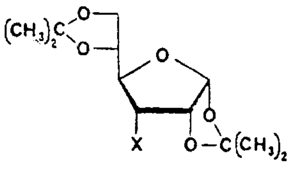
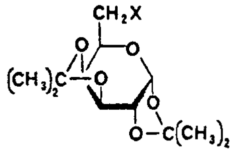
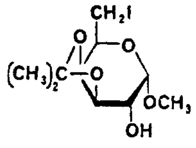
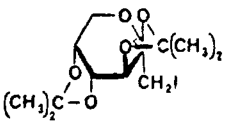
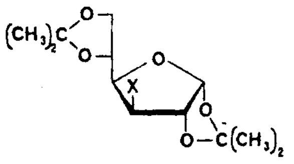
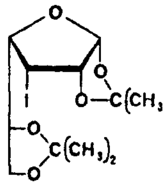
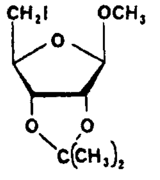
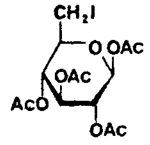
(23) Flechtner, T. W. *Carbohydr. Res.* **1979**, *77*, 262.

Table IV

starting material	product	reaction time, h	% yield	ref to previous synthesis of deoxyhalogeno sugar
	 17, 26, 27			
9	17, X = I	18	84	1, 12
	26, X = Br	18	42[a]	13[b]
	27, X = Cl	18	22[a]	13[b]
	 18, 28, 29			
10	18, X = I	2	94	4
	28, X = Br	2	89	14
	29, X = Cl	2	87	14
	 19			
11	19	2	62	15
	 20			
12	20	15	99	16
	 21, 30, 31			
13	21, X = I	12	87	17
	30, X = Br	12	96	14
	31, X = Cl	12	85	14
	 22			
14	22	5	81	18[b]
	 23			
7	23	[c]	87	19
25	23	1	95	19
	 24			
8	24	[c]	97	20

[a] Compound 26 also formed. [b] Reference is to deoxy sugar synthesis. [c] Procedure for unstable triflates used.

reaction take place in the presence of ketal and ester protecting groups and are not accompanied by rearrangement. Both primary and secondary hydroxyl groups can be replaced. Elimination reactions are rare and are completely avoided when iodide ion is the nucleophile.

Experimental Section

General Procedures. Synthesis procedures are described below in general form. ^{1}H NMR spectra were obtained (CDCl$_3$; (CH$_3$)$_4$Si, 0 ppm) from a Varian T-60 spectrometer (coupling constants, J, are given in hertz; s, d, t, and m indicate singlet, doublet, triplet, and multiplet, respectively). Mass spectra were measured on a Finnigan 1015-D mass spectrometer, using electron impact (ionizing voltage of 70 eV).

Synthesis of the Triflate Esters. A 100-mL two-neck round-bottom flask equipped with two addition funnels was charged with pyridine (0.43 mL, 5.5 mmol) and 20 mL of methylene chloride. A solution of triflic anhydride[24] (0.86 mL, 5.11 mmol) dissolved in 10 mL of methylene chloride was placed in one addition funnel. The sugar (2.55 mmol) dissolved in 10 mL of methylene chloride was placed in the other addition funnel. The flask was cooled to -10 °C in an ice/acetone bath and the triflic anhydride solution added dropwise. A thick white precipitate began to form during the addition. After addition was complete, the suspension was allowed to stir for an additional 10 min. The sugar solution was added dropwise and stirring continued for an additional 1.5 h. The reaction mixture was poured into 50 mL of ice-water, the layers were separated, and the aqueous layer was extracted with two 50-mL portions of methylene chloride. The combined extracts were dried over sodium sulfate and the solvent was removed in vacuo. Hexane extraction followed by in vacuo solvent removal gave the triflate ester. Spectral data on the triflates 9-14 are given in Tables II and III. References to previous preparations of these compounds or to the partially protected carbohydrates from which they were prepared is given in Table I. Triflate formation was quantitative.

Synthesis of Deoxyhalogeno Sugars from Stable Triflates. A 100-mL round-bottom flask was charged with the triflate ester (3.00 mmol), tetrabutylammonium halide (6.0 mmol), and 50 mL of benzene. A reflux condenser and drying tube were attached and the reaction mixture was refluxed for the time shown in Table IV. The mixture was then cooled and the benzene removed in vacuo. The resulting brown residue was extracted with three 50-mL portions of hot hexane. The combined extracts were filtered and the hexane was distilled in vacuo to give the deoxyhalogeno sugar. Product yields and references to independent syntheses of these deoxyhalogeno compounds used to obtain authentic samples are given in Table IV. The ^{1}H NMR spectra are given in Table II and the mass spectra in Table III.

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(24) Fieser, M.; Fieser, L. F. "Reagents for Organic Synthesis"; Wiley: New York, 1974; Vol. 4, p 533.

Synthesis of Deoxyiodo Sugars from Unstable Triflates. A 100-mL round-bottom flask containing 3.00 mmol of the partially protected carbohydrate, 6.00 mmol of tetrabutylammonium iodide, 6.5 mmol of pyridine, and 50 mL of dichloromethane was cooled to −78 °C and maintained there with stirring during the dropwise addition of a solution of 6.00 mmol of triflic anhydride in 20 mL of dichloromethane from a pressure-equalizing dropping funnel. The entire system was closed before cooling. After the triflic anhydride addition, the reaction mixture was allowed to warm to room temperature over the period of 1 h and then it was extracted with 150-mL portions of water, 5% sodium bisulfite, 5% sodium bicarbonate, and water. The organic phase was dried over sodium sulfate and the solvent removed in vacuo to produce the dark colored deoxyiodo sugar. This material was purified by passing it through a 2.5 × 10 cm column of 200–325-mesh silica gel slurry packed in 1:1 ether–hexane and eluted with 250 mL of this solvent mixture. Product yields and reference to independent syntheses of **23** and **24** used to obtain authentic samples are given in Table IV. The ^{1}H NMR spectra are given in Table II and the mass spectra in Table III.

Registry No. 1, 582-52-5; **2**, 4064-06-6; **3**, 40269-01-0; **4**, 20880-92-6; **5**, 2595-05-3; **6**, 14686-89-6; **7**, 4099-85-8; **8**, 13100-46-4; **9**, 55951-93-4; **10**, 71001-09-7; **11**, 74925-14-7; **12**, 74925-15-8; **13**, 55951-90-1; **14**, 74925-16-9; **17**, 67337-61-5; **18**, 4026-28-2; **19**, 71732-12-2; **20**, 38084-03-6; **21**, 14260-27-6; **22**, 74958-55-7; **23**, 38838-06-1; **24**, 7468-48-6; **25**, 74925-17-0; **26**, 74958-56-8; **27**, 74925-18-1; **28**, 38838-08-3; **29**, 13454-63-2; **30**, 14260-29-8; **31**, 32785-94-7; **32**, 2774-28-9; tetrabutylammonium iodide, 311-28-4; tetrabutylammonium bromide, 1643-19-2; tetrabutylammonium chloride, 1112-67-0; triflic anhydride, 358-23-6; tresyl chloride, 1648-99-3.

Total Synthesis of Steroid Hormones. Efficient Stereocontrolled Synthesis of 17-Methoxy-6-oxo-*D*-homo-18-nor-5β-androsta-2,13,15,17-tetraene[1]

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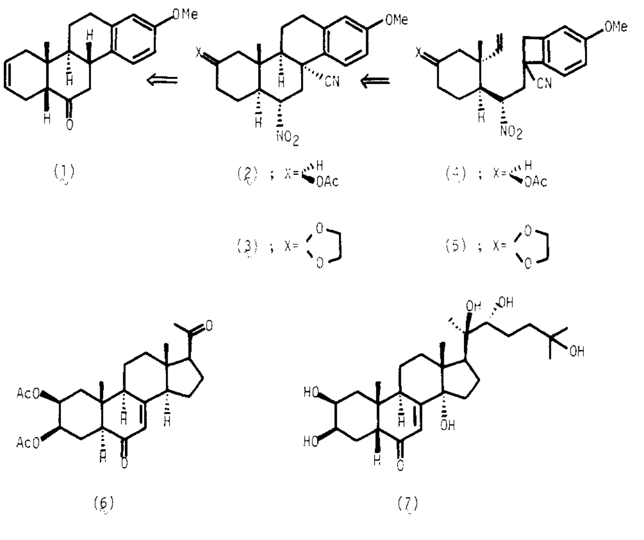
A stereoselective synthesis of 17-methoxy-6-oxo-*D*-homo-18-nor-5β-androsta-2,13,15,17-tetraene (**1**) has been achieved through the key step of thermolysis of 5-acetoxy-2-[2-(1-cyano-4-methoxybenzocyclobutenyl)-1-nitroethyl]-1-ethenyl-1-methylcyclohexane (**4**) and 2-[2-(1-cyano-4-methoxybenzocyclobutenyl)-1-nitroethyl]ethenyl-5,5-(ethylenedioxy)-1-methylcyclohexane (**5**). An alternative synthesis of **1**, starting from 3,3-(ethylenedioxy)-17-methoxy-*D*-homo-18-nor-androsta-5,8,13,15,17-pentaene (**33**), was carried out to confirm its structure.

Intramolecular cycloaddition of *o*-quinodimethanes has proven to be one of the most promising methods for the synthesis of polycyclic natural products, including A-ring aromatic steroids. Several groups, including our own,[2–6] have reported the successful application of the method for the synthesis of physiologically active target molecules, and we have recently extended it to achieve the stereoselective synthesis of D-ring aromatic steroids.[1,7] Our conversion of the latter to pregnane-type steroids has provided a new synthetic entry in this field. D-ring aromatic steroids with Δ^2 and 6-oxo groups are considered to be general intermediates for the synthesis of insect molting hormones, connecting with our D-ring transformation[8] and the conversion of pregnane-type steroid **6** into β-ecdysone (**7**).[9] Here we report a stereoselective total synthesis of 17-methoxy-6-oxo-*D*-homo-18-nor-5β-androsta-2,13,15,17-tetraene (**1**), via **2** and **3**, by thermolysis of benzocyclobutenes **4** and **5** (Scheme I).

Scheme I



As a preliminary experiment, synthesis of the olefinic benzocyclobutene **4** was carried out as follows. To olefinic ester **9** [prepared by 1,4-addition of vinylmagnesium bromide to Hagemann's ester (**8**)[10] in the presence of cuprous iodide] was converted into the tosylate **13**, via the diol **11** and the hydroxy tosylate **12**, by successive reduction with lithium aluminum hydride in tetrahydrofuran, tosy-

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(1) A part of this research has been reported as a communication: T. Kametani and H. Nemoto, *Tetrahedron Lett.*, 3309 (1979).

(2) For a recent review of intramolecular cycloaddition reactions of *o*-quinodimethanes, see W. Oppolzer, *Synthesis*, 793 (1978).

(3) T. Kametani, H. Nemoto, M. Tsubuki, and M. Nishiuchi, *Tetrahedron Lett.*, 27 (1979).

(4) T. Kametani, H. Nemoto, M. Tsubuki, G.-E. Purvaneckas, M. Aizawa, and M. Nishiuchi, *J. Chem. Soc., Perkin Trans. 1*, 2830 (1979).

(5) W. Oppolzer, D. A. Roberts, and T. G. C. Bird, *Helv. Chim. Acta*, **62**, 2017 (1979).

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