graphic separation. This conclusion is supported by the fact that no alcohols were detected in the solvolysis products of **2b** even though the same solvent was used in each case.

Experimental Section[10]

3β-Chloro-5α-cholestan-6α-ol (2a).—To a solution of cholesteryl chloride[11] (**1a**) (24.3 g, 60 mmol) in 300 ml of THF was added sodium borohydride (10 g). The mixture was cooled to 0° and stirred under nitrogen as a solution of boron trifluoride etherate (50 ml) in THF (50 ml) was added dropwise over 45 min. After stirring at 25° for 12 hr, the mixture was cooled to 0° and 100 ml of 12% NaOH was added cautiously during 1 hr followed by 75 ml of 30% hydrogen peroxide over 20 min. The mixture was stirred at 25° for 1 hr, diluted with water, and extracted with ether (two times). The combined ether extracts were washed with water (two times), 5% $NaHSO_3$ (two times), and water, dried ($MgSO_4$), and filtered. Ether evaporation under reduced pressure gave a colorless syrup which crystallized from aqueous acetone containing methanol. Three crystallizations from aqueous acetone gave 11.2 g (40%) of the stanol **2a**: mp 101–102° and 110–110.5°; $[\alpha]^{23}D$ +50° (lit.[6] mp 116–118°; $[\alpha]^{23}D$ +52°); ir (CS_2) 3625 (OH), 758 cm^{-1} (equatorial CCl). Treatment of **2a** with acetic anhydride afforded the acetate **2c** which crystallized from acetone–methanol (1:1), mp 97–99°, $[\alpha]^{23}D$ +59° (lit.[6,12] mp 97–99°).

6α-Tosyloxy-3β-chloro-5α-cholestane (2b) was prepared in 97% yield from **2a** in the usual manner. Two crystallizations from acetone gave pure material: mp 162.5–163°; $[\alpha]^{23}D$ +54°; ir (CS_2) 1180 and 1165 (sym S=O), 758 cm^{-1} (equatorial CCl).

Anal. Calcd for $C_{34}H_{53}ClO_3S$: C, 70.73; H, 9.25; Cl, 6.14. Found: C, 70.79; H, 9.40; Cl, 6.25.

3β-Toyloxy-5α-cholestan-6α-ol (3a).—Cholesteryl tosylate[13] (**1b**) (81.1 g, 150 mmol) in THF (700 ml) was hydroborated with sodium borohydride (10 g) and boron trifluoride etherate (30 ml in 25 ml of THF) according to the procedure for **2a**. Subsequent treatment with 12% NaOH (100 ml) and 30% hydrogen peroxide (50 ml) followed by the usual work-up and crystallization from ethanol afforded **3a** (64.7 g, 80%) as colorless crystals: mp 135–135.3°; $[\alpha]^{23}D$ +23°; ir ($CHCl_3$) 3625 (OH), 1188 and 1175 cm^{-1} (sym S=O).

Anal. Calcd for $C_{34}H_{54}O_4S$: C, 73.07; H, 9.73; S, 5.73. Found: C, 72.76; H, 9.96; S, 5.74.

3α-Chloro-5α-cholestan-6α-ol.—A mixture of **3a** (560 mg, 1 mmol), tetraethylammonium chloride (331 mg, 2 mmol), and potassium carbonate (138 mg, 1 mmol) in 30 ml of DMF was refluxed for 25 min. After cooling to 25°, water was added and a white solid was obtained upon additional cooling to 0°. The solid was taken up in ether and filtered to remove the inorganic salts, and the ether was evaporated to give a colorless syrup which was crystallized twice from methanol affording 275 mg (65%) of the stanol **4a**: mp 156–157°; $[\alpha]^{23}D$ +36°; ir (CS_2) 3625 (OH), 720 cm^{-1} (axial CCl). Treatment of **4a** with acetic anhydride gave the acetate **4c**, which crystallized from methanol: mp 100–100.8°; $[\alpha]^{23}D$ +45°; ir (CS_2) 1735 (ester C=O), 1243 (ester CO), 720 cm^{-1} (axial CCl).

6α-Tosyloxy-3α-chloro-5α-cholestane (4b) was prepared in 83% yield from **4a** in the usual manner. The analytical sample was obtained after two crystallizations from 90% aqueous acetone: mp 139–139.5°; $[\alpha]^{23}D$ +28°; ir (CS_2) 1182 and 1162 (sym S=O), 720 cm^{-1} (axial CCl).

Anal. Calcd for $C_{34}H_{53}ClO_3S$: C, 70.73; H, 9.25; Cl, 6.14. Found: C, 70.92; H, 9.12; Cl, 6.33.

Product Analysis.—The products resulting from the solvolysis of both **2b** and **4b** at 90° in acetic acid solutions containing 0.04 *M* sulfonate, 0.08 *M* sodium acetate, and 0.08 *M* acetic anhydride were isolated by the usual ether extraction technique followed by chromatography over 70–325 mesh silicic acid.[7] Products were identified by comparison of their melting points and infrared spectra with those of authentic samples. The results obtained are listed in Table III.

(10) Experimental details have been given elsewhere.[5]

(11) O. Diels and P. Blumberg, *Ber.*, **44**, 2847 (1911).

(12) Professor Shoppee has kindly informed us that the originally reported rotation is in error, and that a new determination gives $[\alpha]D$ +63°, in chloroform. A mixture melting point with a sample generously supplied by Professor Shoppee showed no depression.

(13) E. S. Wallis, E. Fernholz, and F. T. Gephart, *J. Amer. Chem. Soc.*, **59**, 137 (1937).

Kinetic Measurements.—The usual sealed ampoule technique was used. The concentration of the sulfonate was 0.002 *M* in anhydrous acetic acid containing sodium acetate (0.004 *M*) and acetic anhydride (0.004 *M*). At appropriate time intervals 3-ml aliquots were quenched in ice water and stored at −15°. At the completion of the run the samples were warmed to 25° and transferred to a 1-cm silica cell whereupon the absorbance was determined using a Gilford Model 2000 spectrophotometer at 261 mμ at a slit width of 0.4 mm according to the method of Swain and Morgan.[14] Rate constants were calculated using a nonlinear least-squares program.[15]

Registry No.—**2a**, 1251-93-0; **2b**, 31406-51-6; **3a**, 28398-68-7; **4a**, 1251-94-1; **4b**, 31354-63-9; **4c**, 31354-64-0.

(14) C. G. Swain and C. R. Morgan, *J. Org. Chem.*, **29**, 2097 (1964).

(15) LSKIN2, written by C. E. De Tar and D. F. De Tar, Florida State University, as modified by Dr. H. A. Hammond, University of California.

Synthesis of Adamantane Derivatives. XVII.[1] Facile Synthesis of Bicyclo[3.3.1]non-6-ene-3-aldehyde and -isopropyl alcohol

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Compared with the well-known ring-cleavage reactions of 1,3-disubstituted adamantanes,[2] those of 2,4-disubstituted adamantanes have been reported only recently.[3-5] In a previous publication[5] we reported that facile fragmentation reactions of 4(e)-methylsulfonoxyadamantan-2-one (**1**) with alkali, bromine, and lithium aluminum hydride afforded bicyclo[3.3.1]non-6-ene-3-carboxylic acid, 2(e)-bromo-4-oxahomoadamantan-5-one, and bicyclo[3.3.1]non-6-ene-3-carbinol (**4**), respectively. In this note, we wish to describe the successful application of this type of fragmentation reaction to the preparation of bicyclo[3.3.1]non-6-ene-3-aldehyde (**3**) and -isopropyl alcohol (**5**).

Treatment of **1** with sodium borohydride afforded a mixture of fragmentation products, from which **3** and **4** were isolated in 53 and 41% yields, respectively, both as oils after chromatography on a silica gel column. Aldehyde **3** exhibited ir absorptions (neat) at 2680, 1730, 1720 (sh), and 1645 cm^{-1} and had a M^+ at *m/e* 150. It gave the 2,4-dinitrophenylhydrazone (DNP) derivative, mp 210–211°. Alcohol **4** was identified as bicyclo[3.3.1]non-6-ene-3-carbinol by comparison of ir and nmr spectra and vpc retention time data with those of an authentic sample.[3,5] The

(1) Part XVI: T. Sasaki, S. Eguchi, and T. Toru, *Tetrahedron Lett.*, 1109 (1971).

(2) (a) H. Stetter and P. Tacke, *Angew. Chem.*, **74**, 354 (1962); (b) H. Stetter and P. Tacke, *Chem. Ber.*, **96**, 694 (1963); (c) C. A. Grob and W. W. Schwarz, *Helv. Chim. Acta*, **47**, 1870 (1965); (d) F. N. Stepanov and W. D. Suchowerchow, *Angew. Chem., Int. Ed. Engl.*, **6**, 864 (1967).

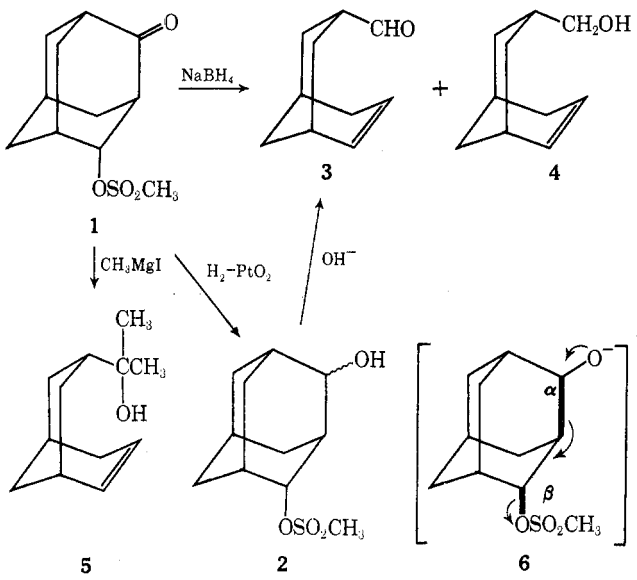
(3) For fragmentation of 4(e)-bromoadamantan-2-one with silver perchlorate to bicyclo[3.3.1]non-6-ene-3-carboxylic acid, see A. C. Udding, H. Wynberg, and J. Strating, *Tetrahedron Lett.*, 5719 (1968).

(4) For the Beckmann fission of adamantan-2-one oxime, see J. G. Korsloot and V. G. Keizer, *ibid.*, 3517 (1969).

(5) For the Schmidt fission of adamantan-2-one, see T. Sasaki, S. Eguchi, and T. Toru, *J. Org. Chem.*, **35**, 4109 (1970).

formation of **3** and **1** can be explained by an alkaline-induced ring fragmentation of the initially formed alcohol **2** as shown in Scheme I. In fact, treatment of

SCHEME I



2 with ethanolic potassium hydroxide afforded aldehyde **3** in 60% yield. Alcohol **2** was easily obtained quantitatively as an oil by catalytic hydrogenation of **1** and had ir absorption bands (neat) at 3540, 3420, 1340 and 1185 cm^{-1} and nmr ($CDCl_3$) signals at δ 5.08–4.88 (m, 1, $CHOSO_2$), 4.15–3.95 (m, 1, CHOH), 3.22 (s, SO_2CH_3), 2.62 (s, 1, OH), and 2.50–1.40 (m, 12, other ring protons).

A further example of the facile ring cleavage of **1** was found in the reaction with Grignard reagent. Treatment of **1** with excess methylmagnesium iodide afforded alcohol **5**, mp 56–57°, in 75.5% yield, which was identified as bicyclo[3.3.1]non-6-ene-3-isopropyl alcohol by elemental analysis and direct comparison of spectral data and melting point with an authentic sample.[6]

The facile fragmentation aptitude of 2,4-disubstituted adamantanes can be understood in terms of the trans-coplanar geometry of the reacting bonds (α and β) in the intermediate as shown in **6**.[5,7] This is in good accordance with the results in the bicyclo[2.2.2]octane system reported recently by Kraus, *et al.*,[8] supporting the Grob hypothesis for fragmentation reactions.[9]

Experimental Section[10]

Reduction of 4(e)-Methylsulfonoxyadamantan-2-one (1) with Sodium Borohydride. Bicyclo[3.3.1]non-6-ene-3-aldehyde (3).—To a stirred solution of **1** (0.40 g, 1.6 mmol) in methanol (30 ml) was added a solution of sodium borohydride (0.90 g, 2.3 mmol) in aqueous methanol (80% v/v, 25 ml) under ice cooling. After stirring was continued for 2 days at room temperature, the mixture was concentrated under reduced pressure in order to remove methanol, diluted with water, acidified with acetic acid, and extracted with ether (five 20-ml portions). The combined ether extracts were dried (Na_2SO_4), and the solvent was removed to give an oily residue which was purified on a silica gel (Mallinckrodt, 100 mesh) column eluting with chloroform. The first fraction gave **3** (0.13 g, 53%) as a colorless oil.

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 80.00; H, 9.71.

Treatment of **3** with 2,4-dinitrophenylhydrazine gave the 2,4-DNP of **3** as red crystals from ethanol–chloroform: mp 210–211°; nmr ($CDCl_3$) δ 11.09 (s, 1, C=NNH), 9.29–8.00 (m, 3, phenyl protons), 7.62 (d, J = 5.5 Hz, 1, CH=N), 6.05 (m, 2, CH=CH), and 2.70–1.40 (m, 11, remaining ring protons).

Anal. Calcd for $C_{16}H_{18}O_4N_4$: C, 58.17; H, 5.49; N, 16.96. Found: C, 58.13; H, 5.41; N, 16.84.

The second fraction gave alcohol **4** (0.10 g, 41%) as a colorless oil; the ir and nmr spectra and vpc retention time were identical with those of an authentic sample.[5]

Catalytic Reduction of 1. 2-Hydroxy-4-methylsulfonoxyadamantane (2).—A solution of **1** (1.0 g, 4.1 mmol) in methanol (20 ml) was hydrogenated in the presence of Adams catalyst (0.5 g) for 15 hr under atmospheric pressure at room temperature. After removal of the catalyst by filtration, the methanol solution was evaporated to dryness under reduced pressure to give **2** as an oil (0.99 g, 99%).

Anal. Calcd for $C_{11}H_{18}O_4S$: C, 53.63; H, 7.37. Found: C, 53.56; H, 7.43.

Alkaline Cleavage of 2 to 3.—Alcohol **2** (0.15 g, 0.61 mmol) was heated in 50% aqueous ethanol (8 ml) containing potassium hydroxide (0.20 g) at 60° for 6 hr. Work-up as usual afforded **3** in 60% yield.

Reaction of 1 with Methylmagnesium Iodide. Bicyclo[3.3.1]non-6-ene-3-isopropyl Alcohol (5).—A solution of **1** (0.50 g, 2.1 mmol) in dry tetrahydrofuran (5 ml) was added to a solution of methylmagnesium iodide in tetrahydrofuran (15 ml) prepared from methyl iodide (2.5 ml) and magnesium (turnings, 1.1 g, 45.3 mg-atoms). After refluxing for 6.5 hr, the cooled reaction mixture was diluted with water (50 ml), acidified with 10% hydrochloric acid, and extracted with ether (four 40-ml portions). Work-up as usual afforded an oily product which was purified on a silica gel column eluting with chloroform to give **5** (0.28 g, 75.5%) as colorless crystals from *n*-hexane: mp 56–57° (lit.[6] mp 56.5–58°); ir (KBr) 3450, 3250, 3160, 1635, and 1140 cm^{-1}; nmr ($CDCl_3$) δ 6.00–5.10 (m, 2, CH=CH), 1.50 (s, 1, OH), 1.14 (s, 6, $OC(CH_3)_2$), and 2.50–0.60 (m, *ca.* 11, other ring protons).

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.77; H, 11.35.

Registry No.—**2**, 31662-18-7; **3**, 31603-46-0; **3** DNP, 31603-47-1; **5**, 28644-53-3.

(6) M. A. McKervey, D. Faulkner, and H. Hamill, *Tetrahedron Lett.*, 1971 (1970). Only the melting point is described herein.

(7) The fragmentation of homoadamantan-4-one systems does not seem to be as facile; *cf.* T. Sasaki, S. Eguchi, and T. Toru, *J. Org. Chem.*, **36**, 2454 (1971).

(8) W. Kraus and W. Rothenwohrer, *Tetrahedron Lett.*, 1007 (1968); W. Kraus and C. Chassin, *Justus Liebigs Ann. Chem.*, **735**, 198 (1970); W. Kraus and C. Chassin, *Tetrahedron Lett.*, 1003, 1113 (1970).

(9) C. A. Grob, *Angew. Chem.*, **81**, 543 (1969); C. A. Grob and P. W. Schiess, *ibid.*, **79**, 1 (1967).

(10) *Cf.* footnote 27 in ref 5.

Tricarbethoxyphosphine

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As part of a program on the synthesis of new flame retardants for cotton, we were interested in preparing the tertiary phosphine containing three carboxamide substituents directly attached to phosphorus, $P(CONH_2)_3$. This compound, which is unknown, was to be prepared by ammonolysis of the corresponding triester, $P(CO_2Et)_3$ (I). Tertiary phosphines which contain one or two carbethoxy substituents are known,[2,3] but the triester I has not been described in the literature.

(1) One of the laboratories of the Southern Marketing and Nutrition Research Division, Agricultural Research Service, U. S. Department of Agriculture.

(2) A. Job and G. Dusollier, *C. R. Acad. Sci.*, **184**, 1454 (1927).

(3) K. Issleib and H. Anhöck, *Z. Naturforsch. B*, **16**, 837 (1961).