Anal. Calcd for $C_8H_{14}O$: C, 76.19; H, 11.11. Found: C, 76.57; H, 10.95.

Vpc analysis showed that the alcohol was more than 99% pure. The infrared spectrum showed absorptions at $\nu_{max}^{CCl_4}$ 3400 (OH), 2960 (CH), 1645 (CH=CH), and 1050 cm^{-1} (CO). The nmr (CCl_4) spectrum showed peaks at τ 9.0–8.1, complex multiplet (9 $C_4H_7CH_2$); 6.47, triplet, J = 6.5 cps (2 $-OCH_2CH_2-$); 5.45, singlet (1 OH); 4.52, (2 CH=CH).

2-(Δ^2-Cyclohexenyl)ethyl *p*-Bromobenzenesulfonate.—Attempts to prepare this brosylate by the common method[19] gave back the alcohol and the acid chloride. Consequently, the alkoxide of the alcohol was prepared (0.69 g of sodium and 3.84 g of alcohol) in anhydrous ether under a nitrogen atmosphere. A solution of *p*-bromobenzenesulfonyl chloride (7.68 g) in anhydrous ether was added dropwise while cooling to −5°. The reaction mixture was stirred for 2 hr at this temperature and then for an additional 6 hr at room temperature. It was then left overnight, the ether solution was filtered, the solvent was removed and the residue was pumped at 0.5 mm for 30 min to remove any volatile products. The crude ester (9.5 g, 91.5%) was purified by several crystallizations, at low temperature, from petroleum ether: mp 10–11°; ir, $\nu_{max}^{CCl_4}$ 2930 (CH_2), 1650 (C=C), 1575 and 1460 (aromatic H), 1395 and 1190 cm^{-1} (OSO_2); nmr ($CDCl_3$), τ 9.0–8.2 (complex multiplet, 9 $C_4H_7CH_2$), 5.87 (triplet, J = 6.5 cps, 2 $-OCH_2CH_2-$), 4.50 (quartet, 2 CH=CH), 2.32 (multiplet, 4 aromatic H).

Ethyl cyclohexylidenecyanoacetate was prepared in 74% yield following Cope's procedure:[20] bp 150–151° (9 mm) (lit.[20] bp 150–151° (9 mm)); $n^{25}D$ 1.4980.

Ethyl cyclohexylcyanoacetate was prepared in 89% yield by catalytic reduction of ethyl cyclohexylidenecyanoacetate in the presence of Pd–C catalyst: bp 144–146° (7 mm); $n^{25}D$ 1.4640.

Cyclohexylacetic acid was prepared in 73% yield by refluxing ethyl cyclohexylcyanoacetate with concentrated hydrochloric acid for 20 hr. Working up the reaction mixture and distillation gave the acid: bp 116–118° (1 mm) (lit.[21] bp 135° (13 mm)); $n^{24}D$ 1.4682.

Ethyl Cyclohexylacetate.—Cyclohexylacetic acid was converted into the ethyl ester according to the usual procedure: bp 82–85° (2 mm) (lit.[21] bp 100° (17 mm)).

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.58; H, 10.58. Found: C, 70.49; H, 10.59.

2-Cyclohexylethyl alcohol was prepared in 94% yield by lithium aluminum hydride reduction of ethyl cyclohexylacetate according to the usual procedure, bp 100–102° (9 mm). The alcohol was converted into the 3,5-dinitrobenzoate derivative, crystallized from petroleum ether: mp 71° (lit.[22] 71–72°).

Anal. Calcd for $C_{15}H_{18}N_2O_6$: C, 55.90; H, 5.59; N, 8.69. Found: C, 55.84; H, 5.53; N, 8.92.

The pure alcohol was regenerated by alkaline hydrolysis of the 3,5-dinitrobenzoate followed by careful distillation through a 6-in. Vigreux column: bp 100–101° (8 mm); $n^{26}D$ 1.4660 (lit.[23] bp 85–87° (6 mm), $n^{20}D$ 1.4670). Vpc analysis showed that the alcohol was homogenous: ir, $\nu_{max}^{CCl_4}$ 3450 (OH), 2975 (CH), and 1055 cm^{-1} (CO); nmr (CCl_4), τ 9.0–8.2 (complex multiplet, 13 $C_6H_{11}CH_2$), 6.5 (triplet, J = 6.5 cps, 2 $-OCH_2CH_2-$), 5.52 (singlet, 1 OH).

2-Cyclohexylethyl *p*-bromobenzenesulfonate was prepared following the procedure employed for the unsaturated ester. The crude product (92% yield) was purified by crystallization from petroleum ether: mp 36° (lit.[2b] mp 37°); ir, $\nu_{max}^{CCl_4}$ 2950 (CH_2), 1645 (C=C), 1580 and 1460 (aromatic H), 1393 and 1190 cm^{-1} (OSO_2); nmr ($CDCl_3$), τ 9–8.2 (complex multiplet, 13 $C_6H_{11}CH_2$), 5.95 (triplet, J = 6.5 cps, 2 $-OCH_2CH_2-$), 2.32 (multiplet, 4 aromatic H).

Product Analysis.—The pure brosylate ester (0.035 mol) was allowed to react in anhydrous acetic acid (500 ml) containing sodium acetate (0.048 mol) for about 14 half-lives. The cooled solution was diluted with 2 l. of water and extracted three times with 200-ml portions of ether. The aqueous layer was diluted again with water, and extracted with ether. The combined ether extract was washed with water, allowed to stand for 2 hr over anhydrous sodium carbonate, and then dried over anhydrous sodium sulfate. The solvent was stripped carefully and the residue was distilled without an attempt at fractionation. The unsaturated ester gave a colorless liquid (91%) with bp 93–102° (2 mm), and the saturated ester gave a colorless liquid (89.5%) with bp 95–103° (3 mm).

Reduction of the Acetolysis Product.—To a slurry of lithium aluminum hydride (1.2 g) in anhydrous ether (30 ml) was added a solution of the solvolysis acetate (0.018 mol) in anhydrous ether. The mixture was refluxed with stirring for 5 hr and left overnight at room temperature. The reaction mixture was decomposed with wet ether and worked up in the usual manner to give the corresponding solvolysis alcohol. The alcohols were purified by distillation without fractionation and subjected to analysis.

Analysis of the Solvolysis Alcohols.—Vpc analysis of the solvolysis alcohol from the unsaturated brosylate showed that it was identical with pure 2-(Δ^2-cyclohexenyl)ethyl alcohol. Similarly the solvolysis alcohol from the saturated brosylate was identical with pure 2-cyclohexylethyl alcohol. Infrared and nmr spectra of the alcohol from the unsaturated brosylate were superimposable upon those of a pure sample: 3,5-dinitrobenzoate, mp 52–53° (from petroleum ether), undepressed when admixed with an authentic sample.

Rate Measurements.—The reagents used were purified and standardized as described in ref 5a. Titrations were carried out with 5-ml microburets using methyl violet indicator (saturated solution in chlorobenzene) and the end point was approached from the acid side. The compound to be solvolyzed was weighed into a volumetric flask and brought up to the mark with sodium acetate solution (0.03–0.04 *M*). The amount of material used was calculated so that the solution would still contain sodium acetate at the end of the reaction. The ampoule technique was employed throughout the rate measurements.

First-order rate constants k (where $k = 1/t \ln (a/a - x)$, a is the initial concentration in moles per liter of the material, t is the elapsed time, and x is the concentration of consumed base) were calculated. A plot of log $(a - x)$ *vs.* t for the solvolysis of the brosylate esters at different temperatures gave straight lines.

Registry No.— Methyl (Δ^2-cyclohexenyl)acetate, 16423-29-3; 2-(Δ^2-cyclohexenyl)ethyl alcohol, 16452-34-9; 2-(Δ^2-cyclohexenyl)ethyl *p*-bromobenzenesulfonate, 16423-30-6; ethyl cyclohexylcyanoacetate, 3212-50-1; 2-cyclohexylethyl *p*-bromobenzenesulfonate, 16423-32-8; Δ^2-cyclohexenylacetic acid, 3675-31-8; 2-(Δ^2-cyclohexenyl)ethyl alcohol 3,5-dinitrobenzoate, 16423-40-8.

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(24) A. A. Youssef, Visiting Research Associate (1965–1966) with Professor L. A. Paquette, Chemistry Department, The Ohio State University.

Synthesis of 2-Methyladenosine and Its 5′-Phosphate

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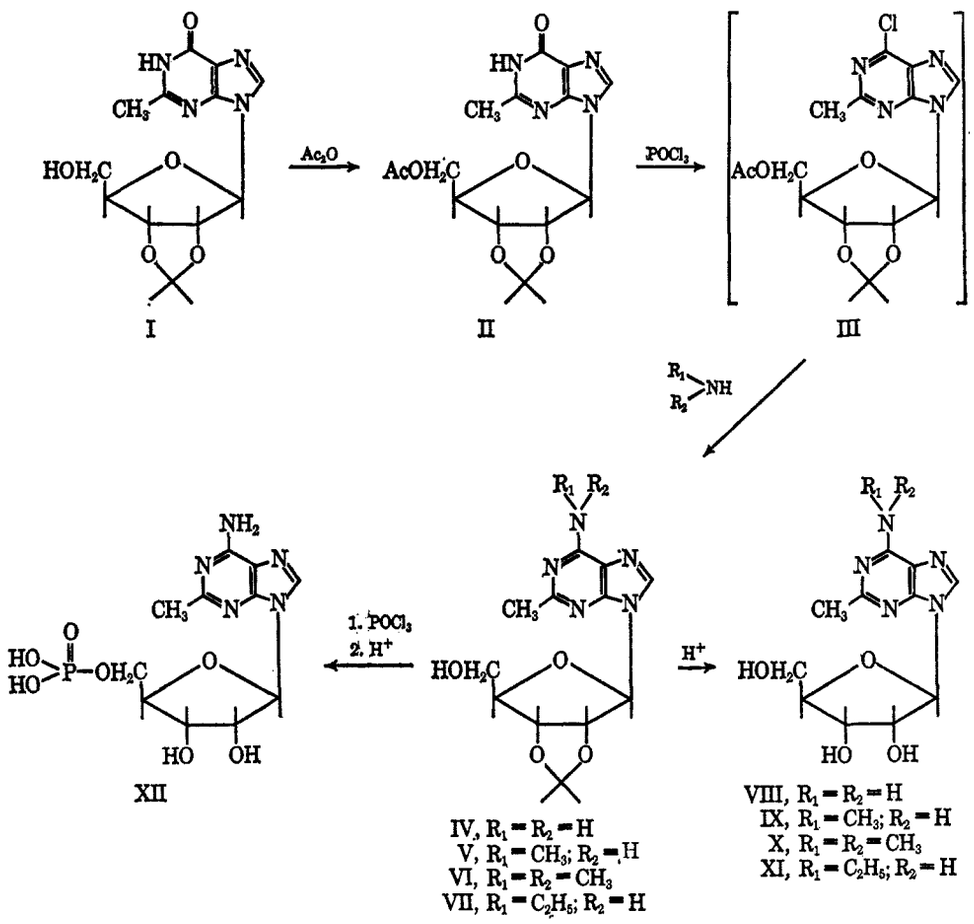
In recent years, a number of methylated purine nucleosides have been detected in transfer ribonucleic acid (RNA) as minor components, and the detection of

SCHEME I



such nucleosides has prompted many synthetic investigations. In previous papers, we have reported on the synthesis of some naturally occurring methylated purine nucleotides in connection with studies on the correlation of the flavoring activity and chemical structure of 5′-nucleotides: for example, N^2-methylguanosine,[1] N^2,-N^2-dimethylguanosine,[1] N^1-methylinosine,[2] and N^1-methylguanosine 5′-phosphates[2] were synthesized starting from 5-amino-1-β-D-ribofuranosyl-4-imidazolecarboxamide.

The present investigation was undertaken in order to synthesize 2-methyladenosine (VIII), its analogs, and 2-methyladenosine 5′-phosphate (XII). Previously, compound VIII was found by Littlefield and Dunn[3] to occur in RNA as a minor component, but the nucleotide XII was not isolated. The classical preparation[4] of VIII involved the condensation of a chloromercuri purine derivative with a blocked halo sugar. However, VIII was not isolated in crystalline form, and, moreover, its physical properties were not described in detail. In contrast, we have chosen 2′,3′-O-isopropylidene-2-methylinosine (I)[5] as a starting material and established a new method for preparing VIII and its analogs.

Compound I was readily acetylated (Scheme I) with acetic anhydride in pyridine to give 2′,3′-O-isopropylidene-5′-O-acetyl-2-methylinosine (II) in 77% yield, which was converted with phosphoryl chloride into 2-methyl-6-chloro-9-(2′,3′-O-isopropylidene-5′-O-acetyl-β-D-ribofuranosyl)purine (III) according to the procedure of Robins, *et al.*[6,7] Compound III was shown to be homogeneous on a paper chromatogram but could not be crystallized. Subsequent amination of III with ammonia in an autoclave at 120° for 3 hr afforded 2′,3′-O-isopropylidene-2-methyladenosine (IV) in 51% yield, from which VIII was obtained by removal of the isopropylidene group. Enzymatically prepared VIII[3] and the synthetic sample were proved to be the same compound by comparison of ultraviolet absorption spectra and R_f values. By a method developed in our laboratories,[8] IV was phosphorylated with phosphoryl chloride in trimethyl phosphate to afford the corresponding 5′-nucleotide. This material was hydrolyzed with acid to give XII, which was characterized by elemental analysis and spectral properties. The yield of XII was 31%.

Recently, numerous adenosine analogs have been detected in nature, some of which have showed significant biological activities. Noteworthy among them are tubercidin,[9] toyocamycin,[10] and puromycin.[11] It is also of interest that 2-methyladenine exhibits anti-

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tumor activity against Adenocarcinoma 755.[12] Then, 2,N^6-dimethyladenosine (IX), 2,N^6,N^6-trimethyladenosine (X), and 2-methyl-N^6-ethyladenosine (XI) as the analogs of VIII were synthesized by the same procedure as described for VIII.

Experimental Section[13]

2',3'-O-Isopropylidene-5'-O-acetyl-2-methylinosine (II).—2',3'-O-Isopropylidene-2-methylinosine[5] (I, 40 g) was dissolved in a mixture of pyridine (450 ml) and acetic anhydride (300 ml), and the solution was allowed to stand at room temperature overnight. After the solvent was removed *in vacuo*, 100 ml of ethanol was added and the mixture was then concentrated. This procedure was repeated several times to decompose acetic anhydride completely. The residue was dissolved in ethanol and allowed to stand at room temperature. The resulting crystals were collected by filtration and recrystallized from ethanol to give 35 g (77%) of pure crystals: mp 151°; $[\alpha]^{25}D$ −11.3° (*c* 1, water); uv, $\lambda_{max}^{pH\ 1}$ 253 mμ (ε 12,400), $\lambda_{max}^{pH\ 6}$ 251.5 mμ (ε 11,600), and $\lambda_{max}^{pH\ 13}$ 258 mμ (ε 12,800).

Anal. Calcd for $C_{16}H_{20}O_6N_4$: C, 52.72; H, 5.53; N, 15.38. Found: C, 52.86; H, 5.67; N, 15.83.

2',3'-O-Isopropylidene-2-methyladenosine (IV).[14]—To a stirred suspension of II (6 g) in phosphoryl chloride (30 ml) was added N,N-dimethylaniline (20 ml) and the mixture was refluxed for 3 min. The color of the solution turned to yellowish green. The reaction mixture was added to an excess of ice water with stirring and the product was extracted six times with 50-ml portions of chloroform. The combined chloroform extracts were washed with 200 ml of cold 1 *N* hydrochloric acid (to remove dimethylaniline), cold water, and 5% sodium hydrogen carbonate. The solution was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure to give a gummy product. This product, which is chromatographically homogeneous, exhibited $\lambda_{max}^{pH\ 1}$ 249.5 and 271 and $\lambda_{max}^{pH\ 13}$ 271 mμ in the ultraviolet spectra. After the above crude III was added to 50 ml of ethanol, the solution was saturated with ammonia at 0° and heated in an autoclave at 120° for 3 hr. The reaction mixture was concentrated *in vacuo* to afford a crystalline product, which was recrystallized from ethanol to give 2.7 g (51%) of pure crystals: mp 202–203°; $[\alpha]^{25}D$ −81.5° (*c* 1, water); uv, $\lambda_{max}^{pH\ 1}$ 259 mμ (ε 12,500), $\lambda_{max}^{pH\ 6}$ 264 mμ (ε 14,300), and $\lambda_{max}^{pH\ 13}$ 264 mμ (ε 14,200).

Anal. Calcd for $C_{14}H_{19}O_4N_5$: C, 52.33; H, 5.96; N, 21.80. Found: C, 52.11; H, 5.89; N, 21.86.

2',3'-O-Isopropylidene-2,N^6-dimethyladenosine (V).—After 3.3 g of II was worked up as described above for IV, the crude III was aminated with 50 ml of 30% methylamine. The crude product was crystallized from water to give 2.1 g (76%) of pure crystals: mp 181°; $[\alpha]^{25}D$ −82.6 (*c* 1, water); uv, $\lambda_{max}^{pH\ 1}$ 265 mμ (ε 15,000), $\lambda_{max}^{pH\ 6}$ 271 mμ (ε 15,700), and $\lambda_{max}^{pH\ 13}$ 271 mμ (ε 16,800).

Anal. Calcd for $C_{15}H_{21}O_4N_5$: C, 53.72; H, 6.31; N, 20.89. Found: C, 53.62; H, 6.36; N, 21.15.

2',3'-O-Isopropylidene-2-methyl-N^6-ethyladenosine (VII).—The crude III obtained from 4 g of II was aminated with 60 ml of 70% ethylamine. After the solvent was removed, the residue was dissolved in a small amount of water and allowed to stand at room temperature. The resulting crystals were filtered and crystallized from water, affording 2.1 g (54%) of the product: mp 123°; $[\alpha]^{25}D$ −78.7° (*c* 1, water); uv, $\lambda_{max}^{pH\ 1}$ 265 mμ (ε 15,300), $\lambda_{max}^{pH\ 6}$ 272 mμ (ε 16,800), and $\lambda_{max}^{pH\ 13}$ 272 mμ (ε 17,800).

Anal. Calcd for $C_{16}H_{23}O_4N_5$: C, 55.00; H, 6.64; N, 20.05. Found: C, 55.09; H, 6.66; N, 20.24.

2-Methyladenosine (VIII).—Compound IV (1 g) was added to 60 ml of water and the solution was adjusted to pH 1.5 with 1 *N* hydrochloric acid. The mixture was heated on the steam bath at 70° for 40 min with stirring to remove the isopropylidene group, cooled, and neutralized with Amberlite IRA-410 (OH^- form). The resin was removed and the filtrate was concentrated to give a crude product. Recrystallization from ethanol afforded 0.61 g (70%) of slightly hygroscopic crystals: $[\alpha]^{25}D$ −66.6° (*c* 1, water); uv,[15] $\lambda_{max}^{pH\ 1}$ 260 mμ (ε 14,000), $\lambda_{max}^{pH\ 6}$ 264 mμ (ε 14,500), and $\lambda_{max}^{pH\ 13}$ 264 mμ (ε 15,200). The nuclear magnetic resonance spectrum in pyridine showed a singlet at 2.65 ppm due to the methyl group.

Anal. Calcd for $C_{11}H_{15}O_4N_5$: C, 46.97; H, 5.38; N, 24.90. Found: C, 46.93; H, 5.49; N, 25.07.

The following compounds were obtained by the same procedure as described for VIII. Their ultraviolet absorption spectra were as expected.

2,N^6-Dimethyladenosine (IX) was recrystallized as a crude product from ethanol. The yield was 71%: mp 179–180°; $[\alpha]^{25}D$ −67.6° (*c* 1, water).

Anal. Calcd for $C_{12}H_{17}O_4N_5$: C, 48.80; H, 5.80; N, 23.72. Found: C, 48.38; H, 5.89; N, 23.57.

2-Methyl-N^6-ethyladenosine (XI) was obtained as an analytically pure sample by recrystallization from water: yield 65%; $[\alpha]^{25}D$ −73.0° (*c* 1, water).

Anal. Calcd for $C_{13}H_{19}O_4N_5$: C, 50.48; H, 6.19; N, 22.64. Found: C, 50.55; H, 6.10; N, 22.41.

2,N,^{6}N^6-Trimethyladenosine (X).—After 3 g of II was treated as usual, the resulting III was aminated with 60 ml of 30% dimethylamine to yield 2',3'-O-isopropylidene-2,N^6,N^6-trimethyladenosine (VI), which failed to crystallize. Then, subsequent removal of the isopropylidene group was carried out as described above. A crude product was obtained by crystallization from ethanol to give 1.4 g (56%) of pure crystals: mp 159°; $[\alpha]^{25}D$ −65.7° (*c* 1, water); uv, $\lambda_{max}^{pH\ 1}$ 272 mμ (ε 16,700), $\lambda_{max}^{pH\ 6}$ 280 mμ (ε 19,500), and $\lambda_{max}^{pH\ 13}$ 280 mμ (ε 19,600).

Anal. Calcd for $C_{13}H_{19}O_4N_5$: C, 50.48; H, 6.19; N, 22.64. Found: C, 50.97; H, 6.54; N, 23.03.

2-Methyladenosine 5'-Phosphate (XII).—Phosphoryl chloride (2.5 ml) was mixed with 15 ml of trimethyl phosphate being cooled at −10° in a three-necked flask equipped with a thermometer and a silica gel drying tube. To this solution was added IV (2.4 g, 7.5 mmol) with stirring while maintaining the temperature below −5°, and the mixture was stirred at −5° for 2.5 hr. Within 30 min, it became clear and turned viscous. The solution was then poured into 500 ml of ice water to decompose the excess of phosphoryl chloride, adjusted to pH 1.5 with alkaline solution, and heated at 70° for 40 min. An aliquot from the solution showed two spots on a paper chromatogram. The major spot was that of XII and the other (minor) was identical with that of VIII. After cooling, the above solution was adjusted to pH 2 and passed through a column (3 × 70 cm) of 300 ml of decolorizing resin[16] to absorb XII. The column was washed with 1 l. of water and the nucleotide was eluted with 0.5 *N* ammonium hydroxide until the eluate became free from ultraviolet-absorbing material. Concentration of the eluate afforded a gummy product which was chromatographically homogeneous. After the crude product was dissolved in 50 ml of water, the solution was adjusted to pH 8.5 and a solution of barium acetate (1.55 g, 5.7 mmol) was added. The resulting precipitate, mainly consisting of barium phosphate, was removed by centrifugation. Addition of one volume of ethanol gave a precipitate of barium salt, which was collected by centrifugation, washed with ethanol, and then dried *in vacuo* at 100° for 2 hr to yield 1.24 g (31%): mp 260° dec; paper chromatography, R_f 0.02 (solvent A), 0.27 (solvent B), and 0.41 (solvent C); the moving distance in paper electrophoresis (10% acetic acid buffer, 800 V/cm, 2 hr), 3.2 cm; uv, $\lambda_{max}^{pH\ 1}$ 259 mμ (ε 10,900), $\lambda_{max}^{pH\ 6}$ 264 mμ (ε 13,200), and $\lambda_{max}^{pH\ 13}$ 264 mμ (ε 13,400). The infrared absorption spectrum showed absorption bands at 1100 (C–O–C) and 980 (P–O–C) cm^{-1}. The nuclear magnetic resonance spectrum in deuterium oxide showed a singlet at 2.75 ppm due to the methyl group.

Anal. Calcd for $C_{11}H_{14}O_7N_5BaP \cdot H_2O$: C, 25.68; H, 3.11; N, 13.62; P, 6.03. Found: C, 25.40; H, 3.09; N, 13.37; P, 5.68.

Registry No.—II, 16545-16-7; IV, 16526-53-7; V, 16526-54-8; VII, 16526-55-9; VIII, 16526-56-0; IX,

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(13) All melting points are uncorrected. Ultraviolet absorption spectra were taken with a Hitachi Type EPS-2 automatic recording spectrophotometer. The nmr spectra were measured with a Varian A-60 using tetramethylsilane as an internal standard. Paper chromatography was carried out on Toyo Filter Paper No. 51 by the ascending method. Solvent systems were A, *n*-butyl alcohol–acetic acid–water, 4:1:1 (v/v); B, *n*-propyl alcohol–ammonia (28%)–water, 20:12:3 (v/v); and C, isopropyl alcohol–saturated ammonium sulfate–water, 2:79:19 (v/v).

(14) This compound was also prepared by reaction of 5-amino-4-cyano-1-(2,'3,-O-isopropylidene-β-D-ribofuranosyl)imidazole with ethyl orthoacetate followed by treatment with ammonia: Dr. T. Meguro, these laboratories, private communication, 1967.

(15) It was reported by Davoll, *et al.*[4] that the compound VIII, obtained by a chloromercuri procedure, showed $\lambda_{max}^{pH\ 1}$ 258 and $\lambda_{max}^{pH\ 13}$ 262.5 mμ.

(16) This decolorizing resin was prepared in our laboratories by copolymerization of metaphenylenediamine, resorcin, and formalin.

16526-78-6; X, 16526-79-7; XI, 16526-80-0; XII·barium salt, 16526-81-1.

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The Addition of Dinitrogen Trioxide to Norbornene[1]

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Schechter, *et al.*[2] have shown that the reaction of dinitrogen tetroxide with norbornene proceeds without skeletal rearrangement of the norbornyl system affording 22% *exo,cis*-2,3-dinitronorbornane, 12% of the *trans*-dinitro compound, and 60% of a mixture of nitronitrites. *exo* attack on the norbornyl system is favored for steric reasons; similar *exo,cis* additions have been observed in radical reactions of *p*-toluenethiol,[3] ethyl bromoacetate,[4] and hydrogen bromide[5] with norbornene. The addition of dinitrogen trioxide to olefins is generally believed to involve an extension of the free-radical mechanism applied to N_2O_4 additions,[6] so it was of interest to examine the course of adduction of norbornene with N_2O_3.

The addition of dinitrogen trioxide to norbornene can be visualized as proceeding through either 2,3, 2,7, or 2,6 addition. The 2,7 addition would be the result of Wagner–Meerwein-type rearrangement of the intermediate radical species. Hydrogen radical transfer in the intermediate would lead to 2,6 product. The course of addition was determined by employing *exo,exo*-5,6-dideuterionorbornene[7] as a substrate for N_2O_3 addition. Were the reaction to proceed without rearrangement to the 2,3 product, the 5,6-methylene protons would remain in *endo* positions in the pseudonitrosite I and nitroxime II (path A, Skeletal rearrangement to a 2,7 product would be accompanied by transformation of the 5,6-methylene hydrogens to *exo* protons in III and IV (path B, Scheme I). Hydrogen transfer in 2,6 addition would result in a deuterium attached to the nitrosated carbon atom in the pseudonitrosite V and oxime deuterium in the nitroxime VI. The results indicate that both the pseudonitrosite and nitroxime possess only *endo* hydrogens at the 5,6 positions. No rearrangement to 2,7 or 2,6 products has taken place; therefore, the reaction must have occurred *via* path A.

The nmr spectrum of the recrystallized nitroxime in deuterioacetone is in accord with structure I, that of *exo,exo*-5,6-dideuterio-3-nitro-2-norbornanone oxime. The oxime proton gives a sharp singlet whose chemical shift varies with concentration. The two bridgehead protons are observed as multiplets at δ 3.0 ppm. The three-proton is highly deshielded, being surrounded by the nitro and oximino groups, and is seen as a doublet at δ 4.8 ppm, with J = 2 cps. This proton is in an *endo* position coupling with the 7-*anti* bridge proton.[8] The bridge protons lie in different magnetic environments; their chemical shifts differ and so do their coupling patterns. A singlet peak at δ 1.4 ppm is attributable to the 5,6-*endo* protons; had they been *exo* in nature, larger coupling would be expected.

The deuterated pseudonitrosite has a high-field spectrum similar to that of the nitroxime. An unrecrystallized, but ether-washed sample of the pseudonitrosite shows a peak (area 2) at δ 5.0 ppm. This is the signal for the protons attached to the carbons bearing nitrogen atoms. This product appears to consist predominantly of the *exo,cis*-nitroso dimer II, since a *trans* configuration would result in *endo* and *exo* protons of different chemical shifts and larger coupling constants. Furthermore, *exo* protons should experience a coupling of 4–5 cps with the bridgehead protons.[8] A two-proton peak at δ 3.0 ppm is assigned to the bridgehead hydrogens and a doublet (area 2, J = 2 cps) at 1.2 ppm is assigned to the 5,6-*endo* protons. The bridge protons are manifested as signals centered at δ 1.5 and 2.3 ppm.

Catalytic reduction of the nitroxime gives a mixture of 2,3-diaminonorboranes. Conversion of the crude diamine product into the dihydrochloride followed by several recrystallizations of this salt affords *trans*-2,3-diaminonorborane dihydrochloride. This substance is identical with the salt prepared by Inglessis.[9] The signals for protons attached to nitrogen-bearing carbon atoms experience different chemical shifts as would be expected for *endo* and *exo* protons. A *cis* configuration would be more symmetrical, leading to the same chemical shift for either proton.

The N_2O_3 addition reaction probably involves initial *exo* attack by nitrogen dioxide. The steric demands of the norbornyl system then direct the combination of the intermediate radical with nitric oxide to favor the *exo,cis* product as in path A.

Experimental Section

Nmr spectra were taken in deuteriochloroform solution with a Varian A-60. Vapor phase chromatography was carried out on an FM-500. Melting points are uncorrected.

Preparation of Norbornene Pseudonitrosite.—A well-stirred solution of 1 mol of norbornene in 500 ml of a 1:1 solution of pentane–ether at −10 to 5° is treated with a mixed stream of nitric oxide at a flow rate of 80 cc/min and air at a flow rate of 40 cc/min. Completion of the reaction is evidenced by the appearance of brown gas above the surface of the reaction mixture, indicating that oxides of nitrogen are no longer being absorbed.

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