graphed on silica gel using methanol–chloroform (1:4) as the eluting agent. The first product to be eluted was a small amount of solid (mp 225–230°, $\lambda_{max}^{H_2O}$ 292 nm). The diazepine nucleoside (100 mg, 33%) was then eluted and was recrystallized from methanol–ether to give a colorless crystalline solid: mp 140–145°; $\lambda_{max}^{H_2O}$ 212 nm; nmr (D_2O) 6.68 [1 H, doublets (J = 7.5 Hz) of AB pattern doublet (J = 14.5 Hz), COC*H*H–], 6.66 [1 H, doublets (J = 1.0 Hz) of doublets (J = 6.5 Hz) of AB pattern doublet (J = 14.5 Hz), COCH*H*–], 6.20 (2 H, H_5'), 4.19 [1 H, doublets (J = 6.5 Hz) of doublets (J = 7.5 Hz) of AB pattern doublet (J = 14.5 Hz), C=C*H*C], 4.14 (1 H, doublet, J = 5.3 Hz, H_1'), 3.57 [1 H, doublets (J = 1.0) of doublet (J = 7.5 Hz), NCH=C].

1-β-D-Ribofuranosyltetrahydro-2*H*-1,3-diazepine-2,4(3*H*)-dione (38) was obtained by hydrogenation of **36** on 10% palladium/carbon in a manner analogous to the preparation of **37**. The product was recrystallized from methanol–ether to give colorless prisms: mp 160–161°; $[\alpha]^{25}D$ −57.5° (c 0.4, H_2O); ir (Nujol) 3450 (NH), 3280 (OH), 1695 and 1660 cm^{-1} (CONCON); uv (H_2O) end absorption only (at pH 7); $\lambda_{max}^{pH\ 11}$ 230 nm; ORD (c 0.1, H_2O) negative plain, $[\phi]_{300}$ −3700, $[\phi]_{250}$ −6400, $[\phi]_{210}$ −18,100.

Anal. Calcd for $C_{10}H_{16}N_2O_6$: C, 46.15; H, 6.20; N, 10.77. Found: C, 45.89; H, 6.28; N, 10.49.

1-(2,3-*O*-Isopropylidene-5-*O*-trityl-β-D-ribofuranosyl)-3-(methoxymethyl)cyclothymine (28). **27** (2.2 g, 3.4 mmol) was stirred with Dowex 1-X8 (30 ml) in methanol at room temperature for 5 hr. The resin was filtered off and the filtrate was evaporated *in vacuo*. Chromatography of the residue on silica gel (benzene–acetone, 10:1) gave **26** as a colorless solid (1.5 g, 76%): ir (Nujol) 1710 and 1670 cm^{-1} (CONCON); uv (MeOH) end absorption; nmr ($CDCl_3$) 8.75–9.25 (2 H, multiplet, H_7), 8.65 (3 H, singlet, CCH_3), 8.42 (3 H, singlet, CCH_3), 8.10 (1 H, multiplet, H_5), 6.65 (3 H, singlet, OCH_3), 6.65 (1 H, multiplet, H_6), 4.86 (2 H, singlet, OCH_2N), 3.99 (1 H, doublet, J = 3.0 Hz, H_1').

Anal. Calcd for $C_{34}H_{36}N_2O_7 \cdot 0.5H_2O$: C, 68.80; H, 6.24; N, 4.72. Found: C, 69.20; H, 6.68; N, 4.78.

1-β-D-Ribofuranosyl-3-(methoxymethyl)cyclothymine (33) was obtained in 100% yield (170 mg) by treating **28** (330 mg, 0.56 mmol) with Bio-Rad AG-50 (H^+) in methanol in a manner analogous to that used in the preparation of **25**. A colorless glassy solid was obtained: ir (Nujol) 1710, 1670 cm^{-1} (CONCON); nmr (D_2O) 8.92 (1 H, multiplet, $H_{7\ endo}$), 8.40 (1 H, multiplet, $H_{7\ exo}$), 7.75 (1 H, multiplet, H_5), 6.67 (3 H, singlet, OCH_3), 6.60 (1 H, multiplet, H_6), 6.32 (2 H, H_5'), 4.85 (2 H, singlet, OCH_2N), 4.03 (1 H, doublet, J = 6.0 Hz, H_1'); uv (H_2O) end absorption.

Preparation and Photochemistry of Pyrimidine Nucleoside Sulfonium Ylides

Takehisa Kunieda[1] and Bernhard Witkop*

Contribution from the National Institute of Arthritis and Metabolic Diseases, National Institutes of Health, Bethesda, Maryland 20014.
Received September 25, 1970

Abstract: Protected anhydropyrimidine nucleosides, such as 2′,3′-*O*-isopropylidene-2,5′-*O*-cyclouridine, 2,2′-anhydro-1-(5-*O*-trityl- or benzoylarabinofuranosyl)uracil, or 2,3′-anhydro-1-(5-*O*-trityl-2-deoxyxylofuranosyl)-thymine, are easily opened by dimethyloxosulfonium methylide to the corresponding stable dimethyloxosulfonium pyrimidine methylides. Further O-methylation of 2′- or 3′-pentose hydroxy groups was observed in the opening of 2,2′-anhydro-1-(5-*O*-trityl-β-D-arabinofuranosyl)uracil with excess dimethyloxosulfonium methylide. Ground-state reactions of the new class of compounds include desulfurization with Raney nickel to 2-methylpyrimidine nucleosides or, after hydrolysis, 2-methyl-4-hydroxypyrimidines, analogs of toxopyrimidine, and hydrolysis to dimethyloxosulfonium 4-hydroxy-2-pyrimidinemethylide, which smoothly reacts with amines, such as dimethylamine, to give 2-(dimethylaminomethyl)-4-hydroxypyrimidine, a reaction which is not possible on the level of the comparable nucleoside. Photolysis of such pyrimidinemethylide nucleosides leads to intramolecular participation, mostly of the C-2′ position, with the formation of 2,2′-methylenecyclopyrimidine nucleosides, such as 3a(α),4(β)-dihydro-4-(hydroxymethyl)-2,2-dimethyl-5a*H*(β)-[1,3]dioxolo[3′,4′]furo[3′,2′:4,5]pyrrolo[1,2-*a*]pyrimidin-9(11*H*)-one, presumably *via* carbene intermediates. Photolysis of dimethyloxosulfonium 4-hydroxy-2-pyrimidinemethylides, in which intramolecular interaction with the sugar moiety is not possible, leads to participation of solvent, water, or methanol, with the formation of 2-hydroxy- or 2-methoxymethyl-4-hydroxypyrimidine, or in the presence of sodium borohydride of 4-hydroxy-2-methylpyrimidine.

Pyrimidine nucleosides have been transformed by inversion of configurations, introduction of functional groups, and rearrangement of the pyrimidine ring *via* anhydronucleosides[2] ever since they have been first synthesized by Todd and coworkers.[3] Anhydronucleosides containing sulfur[4,5] and nitrogen[6] as the bridging heteroatoms are but variations on the general theme of modifications of nucleosides by this approach. In this paper we describe exploratory synthetic routes to 2-substituted and 2,2′-carbocyclic pyrimidine nucleosides starting from anhydronucleosides *via* oxosulfonium methylides of pyrimidine nucleosides. Several dimethyloxosulfonium ylides stabilized by carbonyl,[7,8] sulfonyl,[9] or other electronegative groups[10–12] have been

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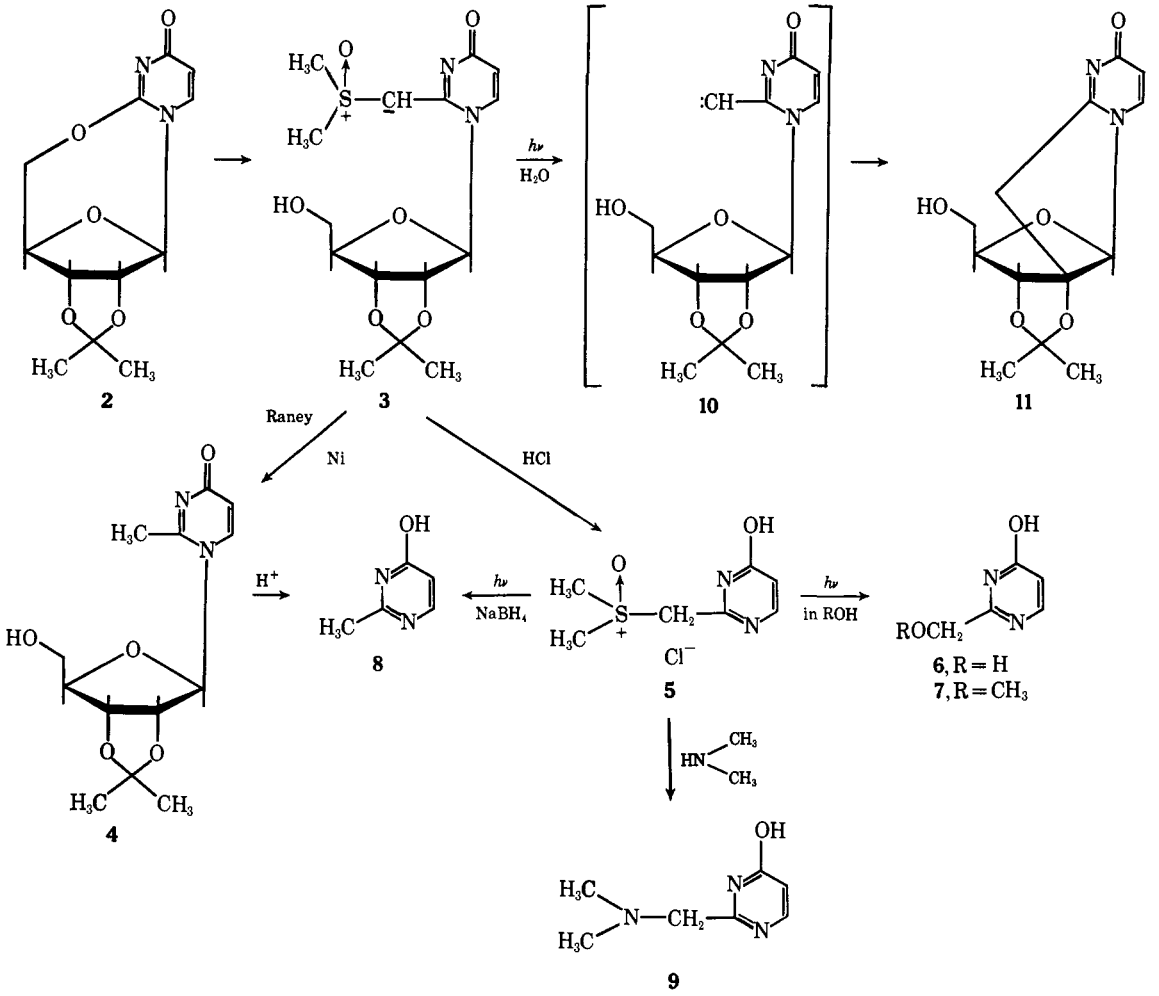
Chart I



isolated. They are of interest with regard to photocleavage of the dipolar sulfur–carbon bond.[7]

We have previously reported on the synthesis of cyclothymine nucleosides,[13] which involves the attack of dimethyloxosulfonium methylide (**1**) on the 5,6-double bond of uridine to afford three-membered bicyclic isomers of thymine.

When, on the other hand, anhydropyrimidine nucleosides were treated with excess ylide in tetrahydrofuran, nucleophilic attack at the C-2 position of the pyrimidine ring took place and stable dimethyloxosulfonium pyrimidinemethylides were obtained in good yield.

In this way, 2′,3′-*O*-isopropylidene-2,5′-*O*-cyclouridine (**2**)[14] was quantitatively converted to dimethyloxosulfonium 1-(2,3-*O*-isopropylidene-β-D-ribofuranosyl)-4-oxo-1,4-dihydro-2-pyrimidinemethylide (**3**, mp 216°, λ_{max}^{MeOH} 278, 236 nm (log ε, 4.38, 4.30)). This structure was established by spectral data, elemental analysis, and by the reactions shown in Chart I. The nmr spectrum (Table I) showed singlet peaks at τ 6.40 and 5.53, in an intensity ratio of 6:1, of which the latter disappeared on addition of D_2O. These peaks are characteristic of a dimethyloxosulfonium methylide structure. Ylide **3** was reductively desulfurized by Raney nickel in aqueous ethanol at room temperature to give 1-(2,3-*O*-isopropylidene-β-D-ribofuranosyl)-2-methyl-4(1*H*)-pyrimidone (**4**), mp 193–194°, $[\alpha]_D$ −90.8° (MeOH), λ_{max}^{MeOH} 242 nm (log ε 4.20). The nmr spectrum (Table II) showed singlet peaks at τ 8.60, 8.35, and 7.40 (1:1:1) attributable to three methyl groups. Acid treatment of ylide **3** easily cleaved the glycosyl bond to give ribose and dimethyloxosulfonium 4-hydroxy-2-pyrimidinemethylide monohydrochloride (**5**), mp 166–168° dec, $\lambda_{max}^{H_2O}$ 268, 232 nm (log ε 3.62, 3.82). The nmr spectrum of ylide **5** exhibited a singlet peak at τ 5.85 and doublet peaks at 3.33 (J = 7.0 Hz) and 1.83 (J = 7.0 Hz), in a ratio of 6:1:1 in D_2O, while singlet peaks at τ 7.43 and 5.50 and doublet peaks at 3.67 and 2.03 (ratio of 6:2:1:1) were observed in DMSO-d_6. A two-proton signal at τ 5.50 is attributable to the $-CH_2-{}^+S(\rightarrow O)<$ group and the assignments made previously should be corrected.

Uv irradiation of **5** in water or methanol with either a low- or high-pressure mercury lamp exclusively led to 2-hydroxymethyl- or 2-methoxymethyl-4-hydroxypyrimidine (**6**, mp 192–194°, λ_{max}^{MeOH} 268, 223 nm; **7**, $\lambda_{max}^{H_2O}$ 260, 228 nm), respectively, with liberation of DMSO and hydrochloric acid. The structure of **6** was established by direct comparison with an authentic sample.[15] The ylide **5**, while stable to sodium borohydride in the dark, on uv irradiation gave 2-methyl-4-pyrimidinol (**8**, hydrochloride, mp 266–268°), which was

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Table I. Nmr Spectral Data for 2-Substituted Pyrimidine Nucleoside Dimethyloxosulfonium Ylides[a]

Compd	O ↑ $(CH_3)_2S^+$–	5-H	6-H	C_1'–H
3[b]	6.30 (s)	4.13 (d, J = 8.0)	2.27 (d, J = 8.0)	4.40 (d, J = 2.0)
	(6.40 (s))[c]	(4.50, d, J = 8.0)[c]	2.43 (d, J = 8.0)[c]	
15[b,c]	6.40 (s)	4.58 (d, J = 8.0)		4.31 (d, J = 4.5)
16[b]	6.33 (s)	4.11 (d, J = 8.0)	2.17 (d, J = 8.0)	4.21 (d, J = 5.0)
17[d]	6.62 (s)			OCH_3, 6.87 (s)
22[c]	6.43 (s)	5-CH_3, 8.37 (broad)		
23[c]	6.42 (s)			

[a] Chemical shifts and coupling constants are given in τ values and hertz, respectively. [b] D_2O solvent. [c] DMSO-d_6 solvent. [d] $CDCl_3$ solvent.

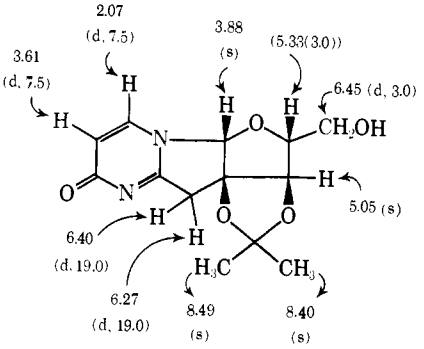
Table II. Nmr Data for 2-Methylpyrimidine Nucleosides[a]

Compd	2-CH_3	5-H	6-H	C_1'–H
4[b]	7.40 (s)	3.64 (d, J = 8.0)	1.90 (d, J = 8.0)	3.93 (broad)
18[c]	7.60 (s)			
19[b]	7.43 (s)	3.64 (d, J = 8.0)	1.83 (d, J = 8.0)	3.80 (d, J = 5.5)
20[d]	7.62 (s)	4.13 (d, J = 8.0)	2.12 (d, J = 8.0)	3.96 (d, J = 5.5)
				O–CH_3, 6.72 (s)

[a] Chemical shifts and coupling constants are given in τ values and hertz, respectively. [b] D_2O solvent. [c] DMSO-d_6 solvent. [d] $CDCl_3$ solvent.

also obtained from nucleoside **4** by acid hydrolysis. This sequence of reactions provides conclusive proof for structure **3** as the dimethyloxosulfonium 2-pyrimidinemethylide structure and for the heterolytic photocleavage of ylide **5**. Ylide **5** with dimethylamine in a dark reaction at room temperature gave 2-(dimethylaminomethyl)-4-hydroxypyrimidine (**9**, mp 155°), while by contrast ylide **3** was completely unreactive to amines, even on warming.

Uv irradiation of **3** in water with a low-pressure mercury lamp gave compound **11** (mp 257–259°, *m/e* 280 (M^+), $[\alpha]^{25}D$ −47.2° (MeOH), 40% yield) which was identified as a novel type of cyclic pyrimidine nucleoside, *viz.*, 3a(α),4(β)-dihydro-4-(hydroxymethyl)-2,2-dimethyl-5a*H*(β)-[1,3]dioxolo[3′,4′]furo[3′,2′:4,5]pyrrolo-[1,2-*a*]-pyrimidin-9(11*H*)-one. The uv spectrum, λ_{max}^{MeOH} 239 nm (log ϵ 4.06), is closely similar to that of **4** and characteristic of a 1-substituted-4(1*H*)-pyrimidone.[16] The nmr spectrum (D_2O) showed an AB pattern at τ 6.40 and 6.27 (J = 19.0 Hz) assignable to the bridging 2,2′-methylene protons and a singlet peak at τ 3.88 belonging to the C_1' proton (**11a**). Although the chemical evidence so far does not preclude the 2,3′-



11a

methylene structure, the less-strained five membered system **11** is preferable on steric and mechanistic grounds, since the intermediate carbene **10**[17] would be expected to react with the most proximal C_2'–H bond of the ribose moiety.

Reaction of the ylide **1** with 2,2′-anhydronucleoside **12**, which is more stable to the nucleophilic attack at the C-2 position,[18] gave two dimethyloxosulfonium 2-pyrimidinemethylides, **15** (46% yield, mp 165–168°, $[\alpha]^{25}D$ +38.4° (MeOH)) and **17** (21% yield, mp 160–170°, $[\alpha]^{25}D$ +49.6° (MeOH)), which had identical uv spectra (λ_{max}^{MeOH} 280, 231 nm) characteristic of sulfonium ylides. Both ylides **15** and **17** on acid hydrolysis gave the hydrochloride **5**, but arabinose was only detected from **15** by paper chromatography, while the O-methylated sugar moiety of **17** could not be identified. The nmr spectra support this observation and show for **17** a three-proton peak at τ 6.87 assignable to an *O*-methyl group in the arabinose moiety.

In a mixture of water and 1,2-dimethoxyethane O-methylation of the 2′-hydroxyl of adenosine becomes preferential.[19] Such selective O-methylation reactions are of interest in connection with the natural occurrence of 2′- (or 3′-) *O*-methyl nucleosides[20] and their effect on tertiary structure.[21]

2,2′-Anhydro-1-(5-*O*-benzoyl-β-D-arabinosyl)uracil (**13**, mp 201–203°, $[\alpha]^{25}D$ +23.5° (MeOH)) prepared from 5′-*O*-benzoyluridine and thiocarbonyldiimidazole[22] with the ylide **1** gave dimethyloxosulfonium 1-β-D-arabinofuranosyl-1,4-dihydro-4-oxo-2-pyrimidinemethylide (**16**, 52% yield, mp 176–178°, $[\alpha]^{25}D$ +141.4° (H_2O), $\lambda_{max}^{H_2O}$ 280, 236 nm (log ϵ 4.26, 4.17)) and 2,2′-anhydro-1-β-D-arabinofuranosyluracil (**14**, 15% yield).[22] The attempt to prepare **16** directly from **14** was unsuccessful, probably because of insufficient solubility in the solvent, tetrahydrofuran.

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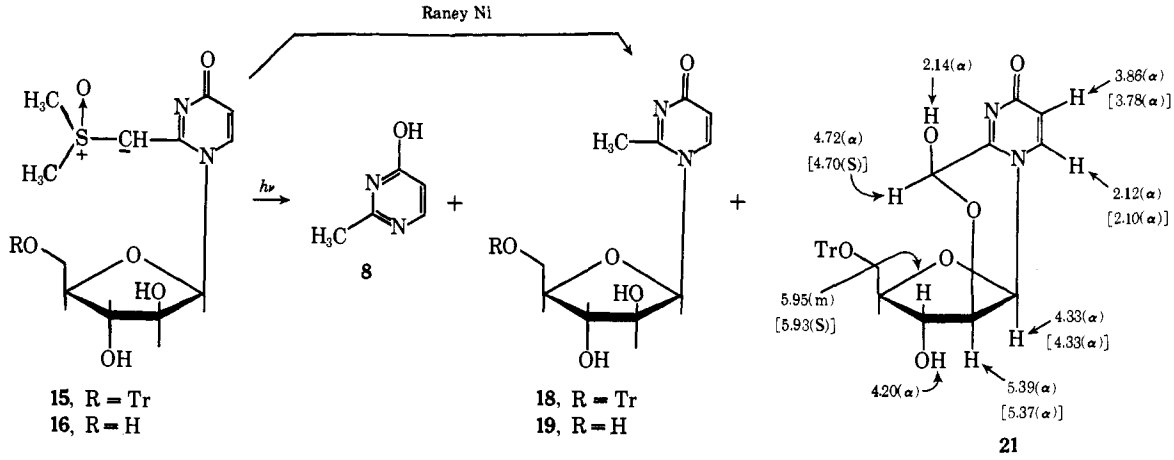
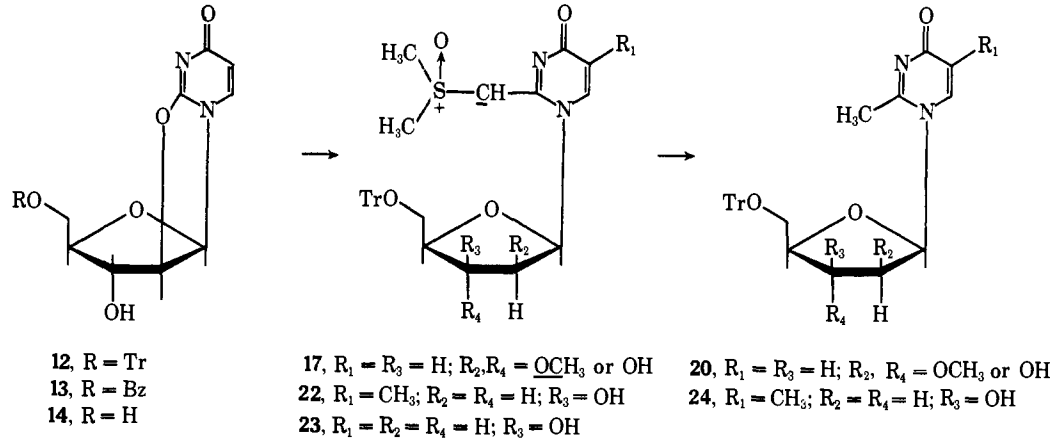
Chart II



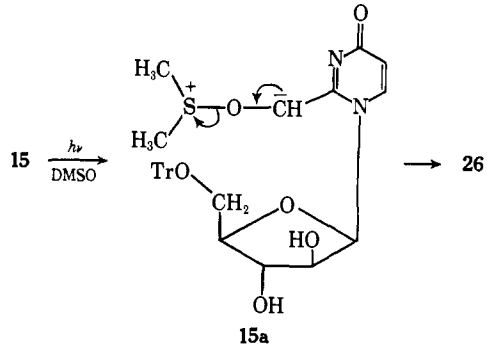


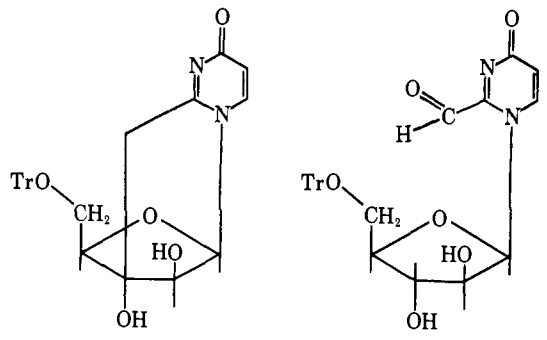
Tr, triphenylmethyl
Bz, benzoyl

Hydrogenolysis of ylides **15**, **16**, and **17** to the corresponding 2-methylpyrimidine nucleosides **18**, **19**, and **20** was achieved within minutes at room temperature by the action of Raney nickel. The nmr spectrum ($CDCl_3$) of **20** (mp 205–206°) showed singlet peaks at τ 7.62 and 6.72 in a ratio of 1:1, indicative of the presence of an *O*-methylarabinose moiety.

When the ylide **15** was irradiated in MeOH with a high-pressure mercury lamp for 40 min, the starting material disappeared and, in contrast to **3**, *several* products were formed. From among these products, 2-methyl-4-pyrimidine (**8**) was characterized as the hydrochloride (mp 260–265°), while the 2-methylpyrimidine nucleoside **18** was only detectable by tlc (silica gel). The major photoproduct was not 2,3′-methylenecyclonucleoside **25** but a compound, **21** (34% yield, mp 200–202°, $[\alpha]^{25}D$ −73.5° (MeOH), λ_{max}^{MeOH} 233 nm (log ϵ 4.26)), which is formulated as the hemiacetal **21**. In agreement with such a structure the nmr spectrum (DMSO-d_6, 100 MHz) showed doublet peaks at τ 4.72 (1 H, J = 6.0 Hz) and 2.14 (1 H, J = 6.0 Hz), which on addition of D_2O changed to a singlet peak and disappeared, suggestive of the presence of a hydroxymethine proton, HO–C–H. A doublet peak at τ 4.20, which disappeared on addition of D_2O, is assignable to H–C_3′–*OH* (Chart II).

Photolysis of ylide **16** gave **8** as the major product (22% yield) and a trace of **19**, in addition to several other photoproducts. Photoproducts **8** and **19** would arise from a possible intermediate carbene, such as **10**, by abstraction of hydrogen from the solvent. If the structure of **21** is correct, it might be formed from an intermediate 2-pyrimidinecarboxaldehyde, **26**, arising from **15** by the oxidizing action of dimethyl sulfoxide,





25 26

liberated in the process of photolysis as shown in **15a**. Ylides **22** and **23**, related to deoxyribosides, were similarly prepared from 2,3′-anhydronucleosides in 30–40% yields. Photolysis of **22** and **23** in MeOH gave several products, which could not be identified.

Such nucleoside oxosulfonium ylides, easily obtained from anhydronucleosides, permit the direct conversion of pyrimidine nucleosides into the biologically important class of compounds related to toxopyrimidines.[23] Two representative ylides, **5** and **16**, at 10^{-4} *M*, so far have shown no activity in preventing the development of Hela and L5178Y cells nor in inhibiting several virus cultures *in vitro*.[24]

Experimental Section

All melting points, determined on a Büchi capillary tube melting point apparatus, are uncorrected. Infrared spectra were measured in Nujol mulls with a Perkin-Elmer Model 237 B spectrometer, ultraviolet spectra with a Cary 15 spectrophotometer, and mass spectra with a Hitachi RMU-60 mass spectrometer. Nmr spectral data were obtained on a Varian A-60 spectrometer, unless otherwise noted. Chemical shifts are given in τ values with TMS as internal standard for spectra in $CDCl_3$ and DMSO-d_6, or sodium 3-(trimethylsilyl)-1-propanesulfonate for spectra in D_2O. Coupling constants (*J*) are shown in hertz. Rotations were measured on a Perkin-Elmer 141 polarimeter.

Irradiations were carried out either with a Hanovia low-pressure (9 W) immersion lamp or with a Hanovia high-pressure mercury lamp (450 W) without filters at 20–30°. In the case of the high-pressure lamp, the distance of the irradiated solution from the light source was 15 mm. Solutions were irradiated in two semicircular quartz vessels of 1 cm lumen and a capacity of 125 ml each. The volume of solution involved and time of irradiation are indicated in the appropriate sections below.

Dimethyloxosulfonium 1,4-Dihydro-1-(2,3-*O*-isopropylidene-β-D-ribofuranosyl)-4-oxo-2-pyrimidinemethylide (3). A mixture of trimethyloxosulfonium chloride (9.0 g) and NaH (1.4 g) was refluxed in dry THF (150 ml) under a stream of N_2 for 2.5 hr. To this ylide solution was added 2′,3′-*O*-isopropylidene-2,5′-*O*-cyclouridine (**2**) (5.0 g), prepared by a modification of the published method.[14] The reaction mixture was gently refluxed for 1 hr and allowed to stand at room temperature overnight. The precipitate was collected by filtration and repeatedly extracted with hot MeOH. The extract was evaporated *in vacuo* to leave a colorless solid (6.3 g), which on recrystallization from MeOH gave the pure ylide as colorless needles: mp 214–216° dec; yield 5.7 g; $[\alpha]^{25}D$ −10.4° (*c* 0.4, MeOH); uv λ_{max}^{MeOH} 278, 236 nm (log ε 4.38, 4.30); λ_{min}^{MeOH} 255 nm (log ε 4.07); ir 3200 (OH), 1630 (C=O), 1580, 1175 (COC), 1120, 1080 (S=O), 1030 (C—O) cm^{-1}.

Anal. Calcd for $C_{15}H_{22}N_2O_6S$: C, 50.27; H, 6.19; N, 7.82; S, 8.94. Found: C, 49.91; H, 6.44; N, 7.64; S, 8.76.

More ylide was obtained from the filtrate by chromatography on silica gel ($CHCl_3$–MeOH, 1:1), which raised the total yield above 90%.

1-(2,3-*O*-Isopropylidene-β-D-ribofuranosyl)-2-methyl-4(1*H*)-pyrimidone (4). A solution of the stable ylide **3** (0.2 g) in 50% aqueous EtOH (20 ml) was treated with active Raney nickel catalyst as obtainable from W. R. Grace & Co. (*ca.* 3 g) at room temperature for 10 min. Tlc indicated complete desulfurization within 1 min. The catalyst was removed by filtration and the filtrate evaporated to dryness *in vacuo*. The residue was crystallized from methanol–ether to give 2-methylpyrimidine nucleoside **4** as colorless needles: mp 193–194°; yield 150 mg (95%); uv λ_{max}^{MeOH} 242 nm (log ε 4.20); ir −3100 (OH), 1640 (C=O), 1600 cm^{-1}; $[\alpha]^{25}D$ −90.8° (*c* 0.33, MeOH).

Anal. Calcd for $C_{13}H_{15}N_2O_5$: C, 55.31; H, 6.43; N, 9.92. Found: C, 55.05; H, 6.22; N, 10.13.

2-Methyl-4-pyrimidinol Hydrochloride (8). A solution of 2-methylpyrimidine nucleoside **4** (50 mg) in EtOH (20 ml), saturated with HCl gas at 0°, was kept at 60° for 2 hr. The solution was evaporated to dryness *in vacuo* and the residue treated with MeOH–ether to give a colorless solid. Recrystallization from EtOH–ether gave the hydrochloride as colorless prisms: mp 260–263° dec; ir −2700 (NH^+), 1710 (C=O), 1660 cm^{-1}; uv λ_{max}^{MeOH} 270, 222 nm; λ_{min}^{MeOH} 242 nm; nmr (D_2O) 7.23 (3 H, s, CH_3), 3.30 (1 H, d, *J* = 7.8 Hz, 5-H), 1.93 (1 H, d, *J* = 7.8 Hz, 6-H).

Anal. Calcd for $C_5H_6N_2O \cdot HCl$: C, 40.96; H, 4.78; N, 19.11. Found: C, 41.03; H, 4.89; N, 19.16.

This compound was identical with the hydrochloride (mp 265–266°) of an authentic sample,[25] prepared from acetamidine and ethyl formylacetate, with regard to ir and nmr spectra.

Dimethyloxosulfonium 4-Hydroxy-2-pyrimidinemethylide Hydrochloride (5). The ribosylpyrimidinemethylide **3** (4 g) was dissolved in EtOH (100 ml) saturated with HCl gas at 0° and the solution stirred at room temperature for 1 hr. The precipitate deposited was collected by filtration and washed with dry ether. Recrystallization from MeOH gave pyrimidinemethylide monohydrochloride **5** (2.6 g, 90%) as colorless crystals: mp 166–168° dec; ir 2700, 1690, 1595 cm^{-1}; uv $\lambda_{max}^{H_2O}$ 268, 232 nm (log ε 3.62, 3.82); $\lambda_{max}^{H_2O}$ 254, 209 nm (log ε 3.58, 3.45); nmr (D_2O) 5.85 (6 H, s, $S(CH_3)_2$), 3.33 (1 H, d, *J* = 7.0 Hz, 5-H), 1.83 (1 H, d, *J* = 7.0 Hz, 6-H); in DMSO-d_6 7.43 (6 H, s, $S(CH_3)_2$), 5.50 (2 H, s, SCH_2), 3.67 (1 H, d, *J* = 7.0 Hz, 5-H), 2.03 (1 H, d, *J* = 7.0 Hz, 6-H).

Anal. Calcd for $C_7H_{11}N_2O_2SCl$: C, 37.75; H, 4.95; N, 12.58. Found: C, 37.97; H, 5.34; N, 12.56.

The mother liquor separated from the precipitate was evaporated *in vacuo*. The residue was dissolved in H_2O and passed through a Dowex 1-X8 (OH^-) column. The presence of ribose was shown by paper chromatography with aniline hydrogen phthalate as a detecting agent (R_f = 0.39, benzene–*n*-butyl alcohol–pyridine–H_2O, 1:5:3:3; R_f = 0.17, EtOAc–H_2O–AcOH, 3:3:1).

2-Hydroxymethyl-4-hydroxypyrimidine (6). An aqueous solution (100 ml) of the ylide hydrochloride **5** (0.3 g) was irradiated with a low-pressure mercury lamp for 3 hr. The solution became strongly acidic and only one product in addition to DMSO was detected by tlc. The solvent was removed *in vacuo* and the product (mp 190–192°) isolated by preparative chromatography on silica gel (MeOH–$CHCl_3$, 2:3). Recrystallization from MeOH or aqueous EtOH gave **6** as slightly yellow crystals (80 mg): mp 192–194°; uv λ_{max}^{MeOH} 268, 223 nm (log ε 3.48, 3.77); λ_{min}^{MeOH} 246 nm (log ε 3.37); ir 3250 (OH, NH), 1635 (C=O), 1120 (C=O) cm^{-1}; nmr (DMSO-d_6) 5.67 (2 H, s, CH_2), 3.86 (1 H, d, *J* = 7.0 Hz, 5-H), 2.19 (1 H, d, *J* = 7.0 Hz, 6-H); mass *m/e* 126 (M^+).

This compound was identical with an authentic sample,[15] prepared by the condensation of hydroxyacetamidine and ethyl formylacetate, with regard to ir, uv, and nmr spectra, as well as behavior on tlc.

2-Methyl-4-hydroxypyrimidine (8) by Photoreduction of 5. An aqueous solution (60 ml) of the ylide hydrochloride **5** (100 mg) and $NaBH_4$ (100 mg) was irradiated for 1.5 hr with a low-pressure mercury lamp. After decomposition of excess borohydride with acetone, the mixture was evaporated *in vacuo* to dryness. The product, purified by preparative chromatography (silica gel, MeOH–$CHCl_3$, 1:2), weighed 40 mg (81%). Treatment with EtOH saturated with HCl gave the hydrochloride, mp 266–268° dec. The ir spectrum was identical with that of an authentic sample.[22]

2-Methoxymethyl-4-hydroxypyrimidine (7) by Photolysis of 5. When the ylide hydrochloride **5** (200 mg) was irradiated in MeOH (250 ml) with a low-pressure mercury lamp, the noncrystalline base was obtained by chromatography (silica gel, $CHCl_3$–MeOH, 1:1); uv $\lambda_{max}^{H_2O}$ 260, 228 nm; $\lambda_{min}^{H_2O}$ 250 nm; nmr (D_2O) 6.51 (3 H, s, CH_3), 5.55 (2 H, s, OCH_2), 3.63 (1 H, d, *J* = 7.0 Hz, 5-H), 2.03

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(24) For these preliminary tests we are indebted to Professor C. Heidelberger, University of Wisconsin, and to Dr. Koert Gerzon, The Lilly Research Laboratories.

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(1 H, d, J = 7.0 Hz, 6-H); mass m/e 140 (M^+) (Calcd for $C_6H_8N_2O_2$: m/e 140.0586. Found: m/e 140.0594). The crystalline hydrochloride had mp 228–231° dec.

2-(Dimethylaminomethyl)-4-hydroxypyrimidine (9). The ylide hydrochloride **5** (0.2 g) was dissolved in 80% methanolic dimethylamine (30 ml) and allowed to stand at room temperature overnight. The product was purified twice by chromatography with $CHCl_3$–MeOH (3:1) and acetone–MeOH (1:1) as developing solvents. The colorless oil (100 mg, 73%) obtained crystallized on standing at room temperature: mp 152–155°; ir 1690 (vs C=O); uv $\lambda_{max}^{H_2O}$ 266, 229 nm; $\lambda_{min}^{H_2O}$ 250 nm; mass m/e 153 (M^+), 110 (base) (Calcd for $C_7H_{11}N_3O$: m/e 153.0902. Found: m/e 153.0907); nmr ($CDCl_3$) 7.66 (6 H, s, $N(CH_3)_2$), 6.53 (2 H, s, NCH_2), 3.69 (1 H, d, J = 6.5 Hz, 5-H), 2.09 (1 H, d, J = 6.5 Hz, 6-H), −1.03 (1 H, s, NH).

Photolysis of 3 to 2,2′-Methylenecyclopyrimidine Nucleoside (11). The ylide **3** (0.9 g) was dissolved in H_2O (250 ml) and irradiated with a low-pressure mercury lamp for 2 hr. After this time tlc showed half of the starting ylide had been converted to the photoproduct. The solvent was removed *in vacuo* and the resulting solid chromatographed on silica gel with $CHCl_3$–MeOH (10:1) as an eluting solvent. The major product crystallized from $CHCl_3$–benzene in slightly yellow crystals (150 mg): mp 257–259°; $[\alpha]^{25}D$ −47.2° (c 0.3, MeOH); uv λ_{max}^{MeOH} 239 nm (log ϵ 4.06); ir 3200 (OH), 1657 (C=O), 1643, 1605, cm^{-1}; mass m/e 280 (M^+); nmr (D_2O) 8.49 (3 H, s, CH_3), 8.40 (3 H, s, CH_3), 6.45 (2 H, d, J = 3.0 Hz, 5′-H), 6.40 (1 H, d, J = 19.0 Hz, 2,2′-CH_2), 6.27 (1 H, d, J = 19.0 Hz, 2,2′-CH_2), 5.05 (1 H, s, 3′-H), 3.88 (1 H, s, 1′-H), 3.61 (1 H, d, J = 7.5 Hz, 5-H), 2.07 (1 H, d, J = 7.5 Hz, 6-H).

Anal. Calcd for $C_{13}H_{16}N_2O_5$: C, 55.71; H, 5.75; N, 10.00. Found: C, 55.77; H, 5.79; N, 9.76.

Dimethyloxosulfonium 1-(5-*O*-Trityl-β-D-arabinofuranosyl)-4-oxo-1,4-dihydro-2-pyrimidinemethylide (15). 2,2′-Anhydro-1-(5-*O*-tritylarabinofuranosyl)uracil (**12**)[22] (8.7 g) was added to the solution of ylide prepared from NaH (2.25 g) and trimethyloxosulfonium chloride (13.5 g) in THF (350 ml) and the mixture was gently refluxed overnight. After removal of the solvent, the residue was dissolved in H_2O and the insoluble part taken up in $CHCl_3$. Two products were isolated by chromatography on silica gel ($CHCl_3$–MeOH, 3:1). Recrystallization from aqueous MeOH of the major product which was eluted out later gave dimethyloxosulfonium 1-(5-*O*-trityl-β-D-arabinofuranosyl)-4-oxo-1,4-dihydro-2-pyrimidinemethylide (**15**) as colorless prisms: mp 165–168° in 46% yield (4.8 g); $[\alpha]^{25}D$ +38.4° (c 0.63, MeOH); uv λ_{max}^{MeOH} 280, 231 nm (log ϵ 4.33, 4.34); λ_{min}^{MeOH} 256 nm (log ϵ 4.00); ir 3400 (OH), 1625, 1570, 1170, 1070, 1040 cm^{-1}.

Anal. Calcd for $C_{31}H_{32}N_2O_6S \cdot 0.5H_2O$: C, 65.31; H, 5.75; N, 4.92; S, 5.63. Found: C, 65.47; H, 5.94; N, 4.77; S, 5.69.

Another O-methylated product, **17** (mp 160–170°, 2.2 g), was obtained as a colorless amorphous solid: $[\alpha]^{25}D$ +49.6° (c 0.6, MeOH); uv λ_{max}^{MeOH} 280, 230 nm (log ϵ 4.34, 4.38); λ_{min}^{MeOH} 256 nm (log ϵ 4.08); nmr ($CDCl_3$) 6.87 (3 H, s, CH_3), 6.62 (6 H, broad, $S(CH_3)_2$).

Anal. Calcd for $C_{32}H_{34}N_2O_6S$: C, 66.88; H, 5.96; N, 4.88; S, 5.57. Found: C, 66.66; H, 5.81; N, 4.81; S, 5.38.

Acid Hydrolysis of 15 and 17. a. The ylide **15** (100 mg) was dissolved in a mixture of 10% HCl (5 ml) and ethanol (5 ml) and kept at room temperature for 3 hr. After removal of the solvents, the residue was crystallized from MeOH–ether to give 2-pyrimidinemethylide hydrochloride **5** as pale-brown needles, mp 163–165°, identical with the hydrochloride obtained from **3**. Arabinose was detected in the desalted (Dowex 1-X8) filtrate by paper chromatography with aniline hydrogen phthalate as a detecting agent (R_f = 0.19, *tert*-BuOH–EtOH–H_2O, 4:1:1; R_f = 0.26, benzene–*n*-BuOH–pyridine–H_2O, 1:5:3:3; no aqueous layer was used).

b. The analogous hydrolysis of **17** gave the ylide hydrochloride **5** and an unidentified sugar moiety with R_f = 0.41 (*tert*-BuOH–EtOH–H_2O, 4:1:1) and R_f = 0.45 (benzene–*n*-BuOH–pyridine–H_2O, 1:5:3:3, no aqueous layer was used).

2-Methyl-1-(5-*O*-trityl-β-D-arabinofuranosyl)-4(1*H*)-pyrimidone (18). An aqueous ethanolic solution of the ylide **15** was desulfurized with Raney nickel (3 g) at room temperature for 10 min. Tlc showed complete hydrogenolysis within a few minutes. After filtration, the filtrate was evaporated to dryness *in vacuo* and the residue was recrystallized from aqueous methanol to give the 2-methyl product **18** (0.3 g, 70%) as colorless crystals: mp 238–239° dec; $[\alpha]^{25}D$ −43.2° (c 0.22, dimethylformamide); ir 3150 (OH), 1645 (C=O), 1620, 1080, 1070 cm^{-1}; uv λ_{max}^{MeOH} 236 nm (log ϵ 4.25); nmr (DMSO-d_6) 7.60 (3 H, s, CH_3).

Anal. Calcd for $C_{29}H_{28}N_2O_5$: C, 71.88; H, 5.83; N, 5.78. Found: C, 71.63; H, 5.82; N, 5.57.

2-Methyl-1-[2-(or 3-)*O*-methyl-5-*O*-trityl-β-D-arabinosyl]-4-oxo-4(1*H*)-pyrimidone (20). A solution of the ylide **17** (1.2 g) in aqueous EtOH (60 ml) was stirred with Raney nickel (wet, 10 g) at room temperature for 30 min. No starting material was detected by tlc. The catalyst was removed by filtration and the filtrate evaporated to dryness. Trituration of the residue with MeOH–ether or acetone–ether gave colorless crystals (860 mg, 84%). Recrystallization from aqueous MeOH gave 2-methylpyrimidine nucleoside **20** as colorless small needles: mp 205–206°; $[\alpha]^{25}D$ +38.6° (c 0.35, MeOH); ir 3200 (OH), 1640 (C=O), 1620 cm^{-1}; uv λ_{max}^{MeOH} 236 nm (log ϵ 4.26).

Anal. Calcd for $C_{30}H_{30}N_2O_5 \cdot 0.5H_2O$: C, 71.00; H, 6.11; N, 5.52. Found: C, 70.63; H, 6.11; N, 5.38.

2,2′-Anhydro-1-(5-*O*-benzyl-β-D-arabinofuranosyl)uracil (13). This compound was prepared from 5′-*O*-benzoyluridine and thiocarbonyldiimidazole in 55% yield, in analogy to the 5′-*O*-trityl derivative.[11] Recrystallization from MeOH gave colorless prisms: mp 201–203°; $[\alpha]^{25}D$ +23.5° (c 0.35, MeOH); ir 3100 (OH), 1730 (ester C=O), 1660 cm^{-1} (amido C=O).

Anal. Calcd for $C_{16}H_{14}N_2O_6$: C, 58.18; H, 4.27; N, 8.28. Found: C, 58.33; H, 4.41; N, 8.22.

Dimethyloxosulfonium 1-β-D-Arabinofuranosyl-1,4-dihydro-4-oxo-2-pyrimidinemethylide (16). The mixture of anhydro compound **13** (1.5 g) and the ylide **1**, prepared from NaH (0.35 g) and trimethyloxosulfonium chloride (2.2 g) in THF, was gently refluxed for 2 hr under a stream of nitrogen and kept at room temperature overnight. The precipitate was collected by filtration and chromatographed on silica gel with $CHCl_3$–MeOH (1:1) as an eluting solvent. The major product was eluted last and crystallized from MeOH as colorless prisms (52% yield): mp 176–178°; $[\alpha]^{25}D$ +141.4° (c 0.4, H_2O); uv $\lambda_{max}^{H_2O}$ 280, 236 nm (log ϵ 4.26, 4.17); $\lambda_{min}^{H_2O}$ 256 nm (log ϵ 3.95); ir 3250 (OH), 1630 (C=O), 1570, 1175, 1040.

Anal. Calcd for $C_{12}H_{18}N_2O_6S \cdot 0.5H_2O$: C, 44.04; H, 5.81; N, 8.56; S, 9.79. Found: C, 44.31; H, 5.60; N, 8.90; S, 10.12.

In addition to **16**, 2,2′-anhydro-1-β-D-arabinofuranosyluracil (**14**) (mp 245–248°; $\lambda_{max}^{H_2O}$ 250, 223 nm; $\lambda_{min}^{H_2O}$ 236 nm) was obtained in 15% (150 mg) yield. This anhydronucleoside was unreactive to the ylide **1** in THF, presumably because of low solubility.

1-β-D-Arabinofuranosyl-2-methyl-4(1*H*)-pyrimidone (19). Ylide **16** was desulfurized with Raney nickel (wet, 4.0 g) in H_2O at room temperature for 10 min. No starting material was detectable at that time. The filtrate was evaporated *in vacuo* and the residue recrystallized from MeOH to give the 2-methylpyrimidine nucleoside **19** as colorless needles: mp 188–190° (170 mg, 75% yield); $[\alpha]^{25}D$ +63.3° (c 0.22, H_2O); uv $\lambda_{max}^{H_2O}$ 242 nm (log ϵ 4.17); $\lambda_{min}^{H_2O}$ 210 nm; ir 3250, 1630, 1060 cm^{-1}.

Anal. Calcd for $C_{10}H_{14}N_2O_5 \cdot 0.5H_2O$: C, 47.81; H, 5.98; N, 11.15. Found: C, 48.13; H, 6.01; N, 11.43.

Photolysis of 15. A solution of 5′-*O*-tritylarabinofuranosylpyrimidinemethylide (**15**) (450 mg) in MeOH (250 ml) was irradiated with a high-pressure mercury lamp for 40 min. After that time the starting ylide had almost disappeared. The solvent was removed *in vacuo* and the residue washed with H_2O. The insoluble pale yellow solid (350 mg) showed at least three spots on tlc (silica gel, $CHCl_3$–MeOH, 10:1). The major product, presumably **21**, was obtained as pale-yellow solid by careful chromatography on silica gel ($CHCl_3$–MeOH, 20:1), followed by preparative thin-layer chromatography (silica gel). Treatment with $CHCl_3$ gave colorless prisms of **21**: mp 200–202°; yield 130 mg (34%); $[\alpha]^{25}D$ −73.5° (c 0.2, MeOH); uv λ_{max}^{MeOH} 233 nm (log ϵ 4.26); ir 3200 (OH), 1640 (C=O), 1620, 1600, 1530, 1070; nmr (DMSO-d_6, 100 MHz) 6.90 (2 H, m), 5.95 (2 H, m), 5.39 (1 H, d, J = 3.0 Hz), 4.72 (1 H, d, J = 6.0 Hz), 4.33 (1 H, d, J = 3.0 Hz), 4.20 (1 H, d, J = 4.0 Hz), 3.86 (1 H, d, J = 8.0 Hz), 2.7 (15 H, aromatic), 2.14 (1 H, d, J = 6.0 Hz), 2.12 (1 H, d, J = 8.0 Hz); in DMSO-d_6–D_2O 6.85 (2 H, m), 5.93 (1 H, s), 5.85 (1 H, m), 5.37 (1 H, d, J = 3.0 Hz), 4.70 (1 H, s), 4.33 (1 H, d, J = 3.0 Hz), 3.78 (1 H, d, J = 8.0 Hz), 2.7 (aromatic), 2.10 (1 H, d, J = 8.0 Hz).

Anal. Calcd for $C_{29}H_{26}N_2O_6$: C, 69.88; H, 5.22; N, 5.62. Found: C, 69.63; H, 5.25; N, 5.49.

The original aqueous filtrate was evaporated *in vacuo*. Tlc showed the residue to contain 2-methyl-4-hydroxypyrimidine (**8**) and a trace of its nucleoside **18** in addition to DMSO. Preparative chromatography on silica gel ($CHCl_3$–MeOH, 1:2), followed by acid treatment, gave 2-methyl-4-hydroxypyrimidine (**8**) hydrochloride (mp 260–265°), whose ir spectrum was identical with that of an authentic sample.

Photolysis of 16. An aqueous solution (500 ml) of the ylide **16** (1.0 g) was irradiated with a high-pressure mercury lamp for 3 hr. After removal of the aqueous solvent, the products were purified by chromatography (silica gel, MeOH–$CHCl_3$, 3:5). The major product was 2-methyl-4-hydroxypyrimidine (100 mg, 22%) which was converted to the hydrochloride and identified by direct comparison with an authentic sample. A small amount of 1-arabinosyl-2-methyl-4(1*H*)-pyrimidinone (**19**) was also obtained.

Dimethyloxosulfonium 1-(5-*O*-Trityl-2-deoxy-β-D-xylofuranosyl)-5-methyl-1,4-dihydro-4-oxo-2-pyrimidinemethylide (22). To the ylide prepared from NaH (0.85 g) and trimethyloxosulfonium chloride (5.5 g) in THF (150 ml) was added 2,3′-anhydro-1-(5-*O*-trityl-2-deoxyxylofuranosyl)thymine[26] (4.5 g) and the mixture was gently refluxed overnight. The precipitate was collected by filtration and washed several times with cold water to leave a colorless solid (2.0 g, 37%), which was recrystallized from MeOH–ether or aqueous EtOH to give colorless crystals: mp 203–205°; $[\alpha]^{25}D$ −9.8° (*c* 20.5, MeOH); ir 3250 (OH), 1640 (C_2), 1550, 1170 cm^{-1}; uv λ_{max}^{MeOH} 280, 233 nm (log ε 4.33, 4.31); λ_{min}^{MeOH} 256 nm (log ε 4.06).

Anal. Calcd for $C_{32}H_{34}N_2O_5S \cdot 0.5H_2O$: C, 67.72; H, 6.17; N, 4.93; S, 5.64. Found: C, 67.54; H, 6.34; N, 4.97; S, 5.21.

The filtered THF solution was evaporated *in vacuo* and the residue was chromatographed on silica gel ($CHCl_3$–MeOH, 5:1) to give another product (1.4 g; λ_{max}^{MeOH} 266 nm; λ_{min}^{MeOH} 246 nm) as a colorless amorphous solid, which was hydrolyzed with HCl to give 3-methylthymine: mp 208–210° (lit.[27] 209–210°); λ_{max}^{MeOH} 264 nm; λ_{min}^{MeOH} 234 nm.

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2,5-Dimethyl-1-(5-*O*-trityl-2-deoxy-β-D-xylofuranosyl)-4-(1*H*)-pyrimidinone (24). Desulfurization of the above ylide **22** (0.2 g) with Raney nickel (2 g) in aqueous EtOH (20 ml) at room temperature for 30 min left a colorless solid (mp 208–213°) which was recrystallized from aqueous methanol to give an analytical sample as colorless prisms: mp 223–225°; uv λ_{max}^{MeOH} 238 nm (log ε 4.20); ir 3200, 1645, 1620 cm^{-1}.

Anal. Calcd for $C_{30}H_{30}N_2O_4$: N, 5.81. Found: N, 5.74.

2,3′-Anhydro-1-(5-*O*-trityl-2-deoxy-β-D-xylofuranosyl)uracil. This compound was obtained from 5′-*O*-trityl-2′-deoxyuridine (5 g) in 65% yield, analogously to the corresponding thymidine.[26] Recrystallization from aqueous EtOH gave colorless needles, mp 138–140°; the uv spectrum showed only end absorption.

Anal. Calcd for $C_{28}H_{24}N_2O_4$: C, 74.32; H, 5.35; N, 6.19. Found: C, 74.46; H, 5.12; N, 6.23.

Dimethyloxosulfonium 1-(5-*O*-Trityl-2-deoxy-β-D-xylofuranosyl)-1,4-dihydro-4-oxopyrimidinemethylide (23). The above anhydrouracil (2.3 g) was treated with the ylide **1** prepared from NaH (0.5 g) and trimethyloxosulfonium chloride (3.3 g) in THF. The product was purified by chromatography on silica gel (MeOH–$CHCl_3$, 5:3) and recrystallized from aqueous EtOH to give the pyrimidinemethylide **23** as colorless crystals (0.84 g, 30% yield): mp 170–175°; $[\alpha]^{25}D$ −7.5° (*c* 0.3, MeOH); uv λ_{max}^{MeOH} 279, 230 nm (log ε 4.37, 4.38); λ_{min}^{MeOH} 255 nm (log ε 4.00); nmr (DMSO-d_6) 6.42 (6 H, s, $S(CH_3)_2$).

Anal. Calcd for $C_{31}H_{32}N_2O_5S \cdot 0.5H_2O$: C, 67.27; H, 5.97; N, 5.05. Found: C, 66.87; H, 5.90; N, 4.98.

Acid treatment in EtOH gave dimethyloxosulfonium 4-hydroxypyrimidinemethylide hydrochloride (**5**), mp 155–157°, identical with an authentic sample.

Hydrogenolysis and Stereochemistry of Photodimers of Thymine and Thymidine

Takehisa Kunieda[1] and Bernhard Witkop*

Contribution from the National Institute of Arthritis and Metabolic Diseases, National Institutes of Health, Bethesda, Maryland 20014.
Received September 25, 1970

Abstract: In analogy to dihydrouracil, -thymine, or 5,6-cyclopropyluracils the cis-syn photodimer of thymine with excess aqueous sodium borohydride at room temperature is easily hydrogenolyzed to the dialcohol 3,4-(α)-*cis*-bishydroxymethyl-3,4(β)-*cis*-dimethyl-1,2(α)-*cis*-dicarbamidocyclobutane (mp 207–208°, 61%), the dicarbinol 4,5-*trans*-dihydroxy-4a,4b-dimethyltetrahydrocyclobuta[1,2-*d*:4,3-*d*′]dipyrimidine-2,7(1*H*,6*H*)-dione (mp 260°, 18%), the monoalcohol 6,7-dimethyl-7-hydroxymethyl-8-ureido-2,4-diazabicyclo[4.2.0]octane-3,5-dione (mp 207°, 5%), and the monocarbinol 4a,4b-dimethyl-5-hydroxyoctahydrocyclobuta[1,2-*d*:4,3-*d*′]dipyrimidine-2,4,7(3*H*)-trione (mp 285–288°, trace). The trans-anti photodimer of thymine gave only one product by complete hydrogenolysis, *viz.*, 2,4-*trans*-bishydroxymethyl-2,4-*trans*-dimethyl-1,3-*trans*-dicarbamidocyclobutane, in analogy to facile ring opening in 0.1 *N* NaOH to *trans*-1,3-dimethyl-2,4-*trans*-dicarbamidocyclobutane-1,3-*trans*-dicarboxylic acid (mp 244°, 80%). The isomeric cis-syn acid was obtained on oxidation of the dialcohol with $KMnO_4$. Catalytic oxygenation (Pt, O_2) of the dicarbinol gave back cis-syn dimer and the monocarbinol (mp 285–288°). The monoalcohol (mp 207°), stable on irradiation, gave on permanganate oxidation a monoacid, *viz.*, 6,7-dimethyl-3,5-dioxo-8-ureido-2,4-diazabicyclo[4.2.0]octane-7-carboxylic acid (mp 238–240°) which on reductive photolysis gave 5,6-dihydrothymine and, presumably, β-ureidoisobutyric acid. The optically active trans-syn photodimers of thymine **3a**, $[\alpha]^{25}D$ +94.1° (H_2O), and **3b**, $[\alpha]^{25}D$ −92° (H_2O), obtained from thymidine dimer precursors, on hydrogenolysis with $NaBH_4$ gave the optically inactive 2,4(α)-*cis*-bishydroxymethyl-2,4(β)-*cis*-dimethyl-1,3(α)-*cis*-dicarbamidocyclobutane, as required by theory.

Part of the radiation damage done to nucleic acids by the action of ultraviolet light is caused by the formation of cyclobutane-type dimers[2,3] and of pyrimidine bases, which play an important role in photoreactivation,[4] photoreversal,[5] and repair processes[6,7] in biological systems. Photodimerizations of pyrimidines have

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