775, 681, 658 cm^{-1}. *Anal.* Calcd for $C_{23}H_{32}O_2Cl_2$: C, 67.14; H, 7.84; Cl, 17.24. Found: C, 67.09; H, 7.79; Cl, 17.84.

3β-Bromoacetoxy-16α,17α-(16′-*exo*,17′-*endo*-dichloro)ethylenepregn-5-en-20-one (5, R = $COCH_2Br$).—3β-Hydroxy-16α,17α-(16′-*exo*,17′-*endo*-dichloro)ethylenepregn-5-en-20-one (**5**, R = H, 1.8 g) dissolved in dry pyridine (2 ml) and anhydrous benzene (500 ml) was treated with 6 ml of a bromoacetyl bromide–benzene mixture (1:2) at room temperature for 7 hr. The reaction mixture was poured into ice–water and the organic layer was washed with dilute hydrochloric acid, aqueous sodium bicarbonate, and water, and then dried (Na_2SO_4). Evaporation of the benzene gave the 3β-bromoacetoxy derivative (**5**, R = $COCH_2Br$), which was recrystallized from methylene chloride–methanol (2.0 g): mp 202–203.5°; $[\alpha]D$ −53°; ν_{max} 1735, 1705, 1225 cm^{-1}; nmr ($CDCl_3$) 0.62 (18-H), 1.02 (19-H), 2.19 (21-H), 3.17 (m, 16-H), 3.80 (s, $BrCH_2CO$), 3.88 (d d, $J_{16,16'}$ = 4.5, $J_{16',17'}$ = 6 Hz, 16′-H), 4.35 (d d, $J_{16,17'}$ = 1.5, $J_{16',17'}$ = 6 Hz, 17′-H), 4.50–4.80 (3α-H), 5.43 ppm (m, 6-H).

Anal. Calcd for $C_{25}H_{33}O_3Cl_2Br$: C, 56.38; H, 6.25; Cl, 13.32; Br, 15.03. Found: C, 56.37; H, 6.35; Cl, 13.55; Br, 15.10.

Registry No.—**4** *p*-bromobenzoate, 29765-32-0; **5** (R = H), 29913-50-6; **5** (R = $COCH_2Br$), 29765-33-1; **5** (R = $COCH_3$), 29765-34-2; **6** (R = $COCH_3$), 29765-35-3.

Acknowledgments.—The authors wish to thank Dr. P. H. Nelson of this Institute for the preparation of the *p*-bromobenzoyl derivative of compound **4** and Mr. John W. Murphy for the spin decoupling experiments on compounds **5** and **6**.

Acetalation and Acetylation of Pyrimidine Nucleosides in Dioxane–Acetonitrile–Hydrogen Chloride

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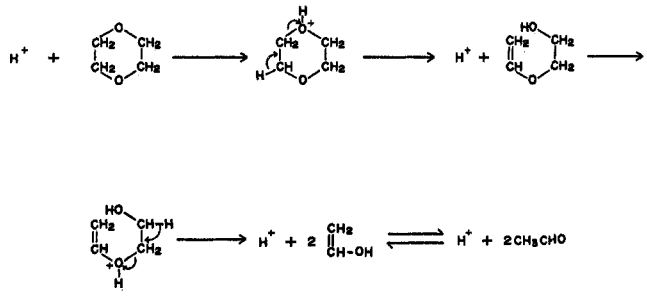
The use of hydrogen chloride in anhydrous dioxane as a catalyst for the conversion of ribonucleosides to corresponding 2′,3′-*O*-alkylidene derivatives has been described by Chládek.[2-4] It has now been found that this catalyst–solvent system, when employed in combination with acetonitrile,[5] effects a smooth transformation of uridine (**1**) to 2′,3′-*O*-ethylideneuridine (**2**). The latter was obtained in 74% yield and was characterized by elemental analysis and spectral (ir and nmr) data. The key step in this conversion is probably the acid-catalyzed cleavage of dioxane to acetaldehyde which in turn reacts with **1** in the usual manner to give the corresponding alkylidene derivative **2**. A possible mechanism of dioxane cleavage in the presence of acid is indicated in Scheme I. In support of the proposed pathway, it has been known for many

SCHEME I



years that the action of sulfuric acid or zinc chloride on dioxane leads to acetaldehyde.[6]

By contrast, thymidine (**3**), which lacks the cis-vicinal diol grouping, reacts with dioxane–acetonitrile–HCl to give 3′,5′-di-*O*-acetylthymidine[7] (**5**) in 56% yield after treatment of the reaction mixture with sodium acetate in water (Scheme II). In this case the formation of a stable cyclic alkylidene derivative is precluded and the acylation of both hydroxy groups most likely takes place through a bis acetimido ether intermediate **4**. The latter is then hydrolyzed during the work-up to **5**. The reaction represents an alternative synthesis of 3′,5′-di-*O*-acetyl-2′-deoxyribonucleosides, employing nonbasic conditions instead of the more usual acetic anhydride–pyridine method.

Uridine (**1**), on treatment with anhydrous hydrogen chloride in acetonitrile and in the absence of dioxane, gave 5′-*O*-acetyluridine (46%) and 2′,3′,5′-tri-*O*-acetyluridine (23%) in addition to other minor products after hydrolysis of the reaction mixture in acetate buffer.

Experimental Section[8]

2′,3′-*O*-Ethylideneuridine (2).—Uridine (**1**, 0.24 g, 1 mmol) dried at 100° (0.1 mm) was shaken with acetonitrile (0.52 ml, 10 mmol) and a 6.5 *M* solution of anhydrous hydrogen chloride in dioxane (2 ml) for 43 hr at room temperature. After standing for an additional 3 days at room temperature, the solution was added dropwise with stirring to 7 *M* ammonium hydroxide (40 ml). The solvents were evaporated to dryness *in vacuo* and the residue was dissolved in acetonitrile (40 ml). The insoluble portion was removed by filtration, the filtrate was evaporated to dryness, and the residue was dried at 50° (0.1 mm) to give a glassy material (**2**) which gradually crystallized. The latter was judged to contain 8% uridine according to paper chromatography (S_1). Substance **2** in water was put on a column of Amberlite resin (OH^- form, 6 × 4 cm) which was eluted with water. The eluate was evaporated to a solid which crystallized from 90% ethanol, affording 0.2 g (74%) of **2**: mp 192–195°; ir ($CHCl_3$) similar to those of 2′,3′-*O*-alkylideneuridines;[9] R_f (S_1) 0.55,

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(2) S. Chládek and J. Smrt, *Collect. Czech. Chem. Commun.*, **28**, 1301 (1963).

(3) S. Chládek in "Synthetic Procedures in Nucleic Acid Chemistry," Vol. I, W. W. Zorbach and R. S. Tipson, Ed., Wiley, New York, N. Y., 1968, p 230.

(4) S. Chládek, ref 3, p 292.

(5) Although the role of acetonitrile in this transformation remains to be clarified, it is possible that the latter serves as an effective scavenger of water under the imposed conditions and thus favorably influences the acetalation equilibrium.

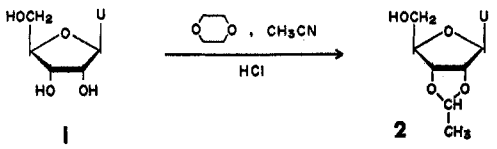
(6) A. Faworski, *J. Russ. Phys. Chem. Soc.*, **38**, 741 (1906).

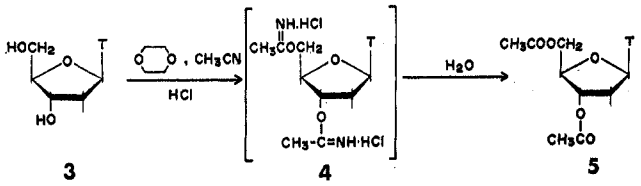
(7) R. E. Belz and D. M. Visser, *J. Amer. Chem. Soc.*, **77**, 736 (1955).

(8) Analyses were performed in the Analytical Department of the Institute of Organic Chemistry and Biochemistry under the direction of Dr. J. Horáček. Melting points were determined on a Kofler block and are uncorrected. All evaporations were carried out *in vacuo;* nmr spectrum was measured on a Varian A-60A spectrometer, using sodium 2,2-dimethyl-2-silapentane-5-sulfonate as an internal standard. Paper chromatography in a descending arrangement was performed on a Whatman No. 1 paper using the following solvent systems: 1-butanol saturated with water (S_1); 1-butanol–acetic acid–water, 5:2:3 (S_2); 2-propanol–concentrated ammonium hydroxide–water, 7:1:2 (S_3); and on Whatman No. 4 paper impregnated with formamide in chloroform as the solvent (S_4). The spots were viewed under the ultraviolet ("Chromatolite").

(9) J. Pitha, S. Chládek, and J. Smrt, *Collect. Czech. Chem. Commun.*, **28**, 1622 (1963).

SCHEME II





(S_2) 0.7, (S_3) 0.59; nmr (CD_3SOCD_3 + D_2O) δ 7.74 (d, 1 H, H_6), 5.69 (two overlapping doublets, 2 H, $H_{1'}$ + H_5), 5.18 (d, 1 H, CH, acetal), 4.74 (m, 2 H, $H_{2'}$ + $H_{3'}$), 4.10 (poorly resolved, overlapped with HDO signal, 1 H, $H_{4'}$), 3.62 (d, 2 H, $H_{5'}$) 1.40 (d, 3 H, CH_3).

Anal. Calcd for $C_{11}H_{14}N_2O_6$: C, 48.89; H, 5.22; N, 10.37. Found: C, 48.75; H, 5.37; N, 10.58.

3′,5′-Di-*O*-acetylthymidine (5).—Thymidine (**3**, 0.12 g, 0.5 mmol) was shaken with acetonitrile (5 ml) and a 6.5 *M* solution of anhydrous hydrogen chloride in dioxane (0.5 ml) for 48 hr at room temperature. Only after 3 hr did the reaction mixture become homogeneous. The solution was added dropwise to an excess of sodium acetate in water and the mixture was extracted with chloroform. The dried organic layer was evaporated to dryness. The syrupy residue solidified after drying at 0.1 mm to give 90 mg (56%) of chromatographically pure solid **5**: mp 123–125° (crystallized from benzene–carbon tetrachloride 2:1 mixture) (lit.[7] mp 123–125°); R_f (S_1) 0.76, (S_4) 0.81. Ammonolysis of **5** gave thymidine as found by paper chromatography (S_1).

Anal. Calcd for $C_{14}H_{18}N_2O_7$: C, 51.53; H, 5.56; N, 8.59. Found: C, 51.52; H, 5.56; N, 8.38.

Reaction of Uridine with Acetonitrile and Anhydrous Hydrogen Chloride.—A suspension of uridine (**1**, 0.12 g, 0.5 mmol) in acetonitrile (10 ml) was saturated with hydrogen chloride, and the solution, which contained a small amount of undissolved solid, was held overnight at room temperature. The reaction mixture was evaporated to dryness; a portion of the crude product was dissolved in 1 *M* triethylammonium acetate (pH 6), and chromatographed in S_1. Authentic samples of **1**, 5′-*O*-acetyluridine, and 2′,3′,5′-tri-*O*-acetyluridine were run simultaneously. Five spots were detected, which were eluted with water and the amount of uv-absorbing material was determined spectrophotometrically at 260 nm (Table I).

TABLE I

Compound	R_f	%[a]
Uridine (1)	0.15	1
5′-*O*-Acetyluridine	0.26	46
Unidentified	0.37	14
Unidentified	0.51	16
2′,3′,5′-Tri-*O*-acetyluridine	0.74	23

[a] Based on sum of the uv absorbances of the five eluted spots.

Registry No.—2, 29765-28-4; **5**, 6979-97-1.

Acknowledgments.—Thanks are due to Dr. Jerome P. Horwitz for valuable comments and to Mr. N. Cvetkov for measuring the nmr spectrum.

A Novel Photochemical Rearrangement–Elimination of an Allylic Alcohol Having a Di-π-methane Structure[1]

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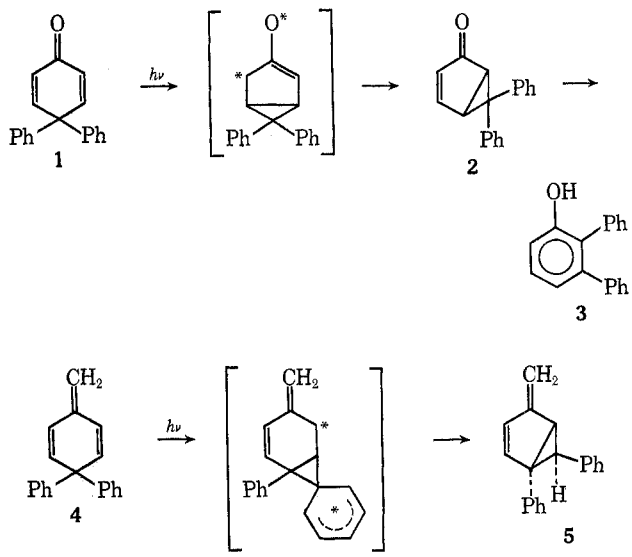
In the course of a study of the di-π-methane rearrangement, the photochemistry of a variety of compounds having a geminal phenyl group allylic to two double bonds has been examined. Generally, compounds having this chromophoric structural feature rearrange to give cyclopropyl products either by 1,3-vinyl–vinyl interaction such as in **1** to **2**,[3] and ultimately **3**, or by 1,3-vinyl–aryl interaction such as in **4** to **5**.[4]



In contrast, when 1-hydroxy-4,4-diphenyl-2,5-cyclohexadiene (**6**) was irradiated in an ethanolic solution with a Vycor filter (λ >210 nm), the only low molecular weight photoproduct was an aromatic hydrocarbon. The product was identified as *o*-terphenyl (**7**) by comparison of its spectra with those of the known compound. A dark control, run parallel with the irradiation, showed no reaction. When the reaction was followed using thin layer chromatography, no buildup of an intermediate could be detected.

The 1,2-phenyl migration in such a system is a common process, but the elimination of water is quite distinctive. Of two possible mechanisms involving intermediates related to structures **2** and **5**, only the alcohol **8** related to the former type has been evaluated owing to synthetic difficulties leading to an alcohol related to **5**, *i.e.*, 1,6-diphenylbicyclo[3.1.0]hex-2-en-4-ol. An intermediate such as **8** could photochemically rearrange

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(2) National Institute of Health Predoctoral Fellow, 1967–1970.

(3) H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, **84**, 4527 (1962).

(4) H. E. Zimmerman, P. Hackett, D. F. Juers, and B. Schroder, *ibid.*, **89**, 5973 (1967).