δ 1.8–2.3 (m, 2, CH_2), 2.0 (s, 3, CH_3), 3.4–4.5 (m, 4, CH_2CH_2P), 7.5–8.1 ppm (m, 15, C_6H_5).

Anal. Calcd for $C_{23}H_{24}O_2PBr$: C, 67.10; H, 5.88; Br, 19.42. Found: C, 66.92; H, 5.84; Br, 19.09.

3-Benzoyloxypropyltriphenylphosphonium Bromide (1b).—Compound **1b** was prepared in a manner similar to that reported in the previous experiment: 76% yield; mp 182–184°; ir ($CHCl_3$) ν 1030 (m), 1070 (m), 1115 (s, CP), 1250 (s), 1170 cm^{-1} (s, ester C=O); nmr ($CDCl_3$) δ 1.9–2.4 (m, 2, CH_2), 3.4–4.3 (m, 2, CH_2P), 4.6 (t, 2, OCH_2), 7.2–8.1 ppm (m, 20, C_6H_5).

Anal. Calcd for $C_{28}H_{26}O_2PBr$: C, 70.99; H, 5.53; Br, 16.87. Found: C, 70.81; H, 5.62; Br, 16.69.

Methyl Cyclopropyl Ketone (5a).—Salt **1a**, 13.4 g (0.03 mol), and potassium *tert*-butylate, 3.4 g (0.03 mol), were allowed to reflux 24 hr in 150 ml of dry *tert*-butyl alcohol. The solution was then cooled and filtered. Methyl cyclopropyl ketone **5a** was identified in this solution by vpc and by treating with 160 ml of 2,4-dinitrophenylhydrazine reagent, which gave orange crystals of the 2,4-dinitrophenylhydrazone, 2.8 g (49%). After recrystallization from ethanol, the crystals had mp 146–148° (lit.[14] 149–150°). Mixture melting point with the authentic sample showed no depression.

Phenyl Cyclopropyl Ketone (5b).—Salt **1b**, 10.1 g (0.02 mol), and potassium *tert*-butylate, 2.2 g (0.02 mol), were treated as described in the previous experiment. The gum obtained was washed well with hexane and the washings were concentrated to give 1.7 g of **5b** (59%) identified by vpc, ir, and nmr comparison with an authentic sample. Washing the hexane-insoluble residue with ether and filtering left a white powder, triphenylphosphine oxide (77%). Cooling the ether filtrate at 0° gave 0.9 g of 1-benzoyl-3-benzoyloxypropyltriphenylphosphorane (**6**), mp 142–146° (17%), one spot by tlc. Repeating this experiment at 20–25° for 36 hr gave 1.55 g of **5b** (53%), identified as described above.

3-Benzoyl-3-benzoyloxypropyltriphenylphosphorane (6): ir ($CHCl_3$) ν 1105 (s, CPO), 1480 (s, O=CC=P), 1720 cm^{-1} (s, ester C=O); nmr ($CDCl_3$) δ 2.1–2.9 (m, 2, CH_2), 3.95 (t, 2, OCH_2), 7.1–7.9 ppm (m, 25, C_6H_5).

Anal. Calcd for $C_{35}H_{29}O_3P$: C, 79.53; H, 5.53. Found: C, 79.62; H, 5.55.

3-Acetoxy-3,4-diphenyl-4-oxobutyltriphenylphosphonium Bromide (1c).—A mixture of 3,4-diphenyl-3-hydroxy-4-oxobutyltriphenylphosphonium bromide[13] (23.2 g, 0.04 mol), NaOAc (0.5 g), and acetic anhydride (12.2 g, 0.12 mol) in 100 ml of dry pyridine was allowed to reflux for 2 hr and stirred at 25° for 8 hr. The mixture was cooled, filtered, and dropped into 1 l. of ether (anhydrous). After decanting the ether, the oily precipitate was boiled briefly in 300 ml of ethyl acetate, which was decanted and recrystallized from chloroform–ether. The yield of **1c** was 18.1 g (73%): mp 221–224°; ir ($CHCl_3$) ν 1115 (s, CP), 1680 (s, ketone C=O), 1745 cm^{-1} (s, ester C=O); nmr ($CDCl_3$) δ 2.3 (s, 3, CH_3), 2.4–4.5 (m, 4, CH_2CH_2P), 7.2–7.9 ppm (m, 25, C_6H_5).

Anal. Calcd for $C_{36}H_{32}O_3PBr$: C, 69.34; H, 5.18; Br, 12.82. Found: C, 69.37; H, 5.28; Br, 12.59.

1-Acetyl-2-benzoyl-2-phenylcyclopropane (5c).—Salt **1c**, 12.5 g (0.02 mol), was suspended in *tert*-butyl alcohol freshly distilled from CaH_2, potassium *tert*-butylate was added (2.8 g, 0.025 mol), and the light yellow solution was allowed to reflux 48 hr. The cooled solution was dropped in 1 l. of hexane and the clear solution decanted. The residual oil was washed with acetonitrile, leaving **8**, 3.2 g (32%), melting point and mixture melting point and spectral data were identical with that of the authentic sample.[13] Concentration of the washings followed by trituration with ether yielded 1.1 g of triphenylphosphine oxide.[3]

Concentration of the original hexane solution and chromatography on florisil gave the cyclopropane **5c**: 2.2 g (42%); only one isomer; mp 100–101.5°; ir ($CHCl_3$) ν 1005 (m), 1180 (s), 1270 (s), 1680 (s, PhC=O), 1700 cm^{-1} (s, CH_3C=O); uv (CH_3OH) λ_{max} 230 mμ (sh, ε 12,400), 258 (17,000); nmr ($CDCl_3$) δ 1.2 (d d, 1, CH_2), 1.8 (s, 3, CH_3), 2.3 (d d, 1, CH_2), 3.2 (d d, 1, CH), 6.7–7.4 and 7.4–7.9 ppm (m, 10, C_6H_5).

Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.08. Found: C, 81.84; H, 6.01.

***cis*- and *trans*-1,2-Dibenzoyl-1-phenylcyclopropane (5d).**—A suspension of 3-benzoyloxy-3,4-diphenyl-4-oxobutyltriphenylphosphonium chloride (1d)[13] (25.6 g, 0.04 mol) was treated with an equimolar quantity of potassium *tert*-butylate as described in the previous experiment and afforded 5-benzoyl-2,2,2,5-tetraphenyloxa-2-phospholane (**8**),[13] 4.2 g (21%), salt **9**, 2.7 g (11%),[13] triphenylphosphine oxide, 5.0 g (45%), and the cyclopropanes **5d**, cis and trans, 6.6 g (51%), in a 23/77 ratio, respectively.

***cis*-1,2-Dibenzoyl-1-phenylcyclopropane** (23%): mp 133–135° (lit.[15] 126°); ir ($CHCl_3$) ν 1100 (s), 1130 (s), 1680 cm^{-1} (s, C=O); uv (CH_3OH) λ_{max} 205 mμ (ε 35,000), 250 (31,500); nmr ($CDCl_3$) δ 2.0 (d d, 1) and 2.5 (d d, 1, CH_2), 3.3 (d d, 1 CH), 7.1–7.6 and 8.2–7.7 ppm (m, 15, C_6H_5).

Anal. Calcd for $C_{23}H_{18}O_2$: C, 84.66; H, 5.52. Found: C, 84.64; H, 5.68.

***trans*-1,2-Dibenzoyl-1-phenylcyclopropane** (77%): mp 121–122° (lit.[15] 123°); ir ($CHCl_3$) ν 1025 (s), 1230 (s), 1270 (s), 1680 cm^{-1} (s, PhC=O); uv (CH_3OH) λ_{max} 295 mμ (ε 24,000), 320 (sh, 8900); nmr ($CDCl_3$) δ 1.6 (d d, 1) and 2.8 (d d, 1, CH_2) 4.1 (d d, 1, CH), 6.9–7.5 and 8.2–7.7 ppm (m, 15, C_6H_5). This compound was found to be identical with an authentic sample prepared by the method of Allen and Barker.[15]

Anal. Calcd for $C_{23}H_{18}O_2$: C, 84.66; H, 5.52. Found: C, 84.86; H, 5.48.

Registry No.—**1a**, 30698-17-0; **1b**, 30698-18-1; **1c**, 30698-19-2; **5c**, 30698-20-5; ***cis*-5d**, 30698-21-6; ***trans*-5d**, 30698-22-7; **6**, 30698-23-8.

Acknowledgment.—We gratefully acknowledge support by a Public Health Service Grant (CA11000) from the National Institutes of Health.

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Photochemical Cycloadducts. VI.[1] The Structure of Tetrafluoroethylene and Dichloroethylene Photoadducts of 3β-Acetoxypregna-5,16-dien-20-one

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In connection with our investigation of the photochemical cycloadditions to conjugated double bonds, we have previously reported the reactions of 3β-acetoxypregna-5,16-dien-20-one (**1**, R = $COCH_3$) with tetrafluoroethylene and *cis*- and *trans*-dichloroethylene.[3] We now wish to report the structures of the products which were not fully characterized.

The photoaddition of tetrafluoroethylene to **1** (R = $COCH_3$) gave three products, two of which have been identified as the α- and β-face adducts **2** and **3**.[3] The structure of the third adduct (mp 180–182°) is now established as **4** by X-ray crystallographic analysis of its 3β-(*p*-bromobenzoate) derivative ($C_{30}H_{33}F_4O_3Br$, space group $P2_12_12_1$ with four molecules per unit cells, a = 22.891, b = 10.692, and c = 11.313 Å[4]).

The photoadditions of certain unsymmetrical olefins to cyclic α,β-unsaturated ketones are generally explained by stepwise mechanisms involving initial car-

(1) For part V, see P. Boyle, J. A. Edwards, and J. H. Fried, *J. Org. Chem.*, **35**, 2560 (1970).

(2) Syntex, S. A., Apartado Postal 2679, Mexico, D. F., Mexico.

(3) P. Sunder-Plassman, P. H. Nelson, P. H. Boyle, A. Cruz, J. Iriarte, P. Crabbé, J. A. Zderic, J. A. Edwards, and J. H. Fried, *J. Org. Chem.*, **34**, 3779 (1969).

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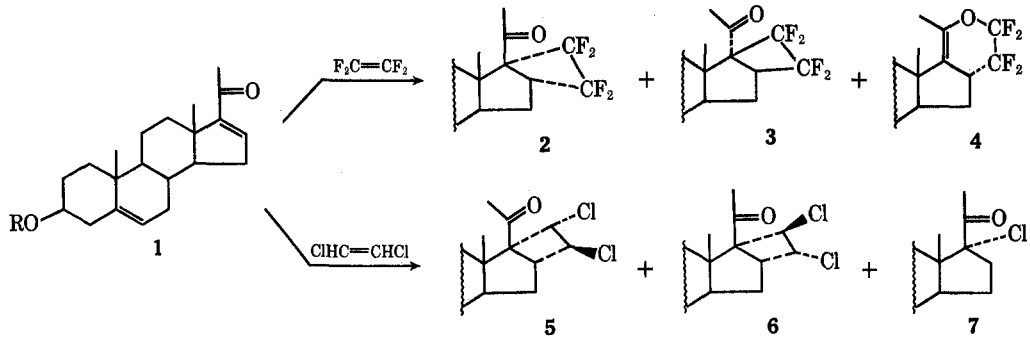

bon–carbon bond formation at either the α[5] or the β position[6] to the carbonyl group. In our case the formation of the β-face adduct **3** and the pyran derivative **4** suggest that the initial bond formation occurs at C-16, *i.e.*, at the β position to the carbonyl function. The resulting diradical intermediate[7] can then lead to products **3** or **4** by ring closure at either C-17 or on the carbonyl oxygen, respectively.

Photochemical cycloaddition of *cis*- or *trans*-dichloroethylene to **1** (R = $COCH_3$) gave a small amount of 17α-chloro-3β-acetoxypregn-5-en-20-one (**7**) and two α-face adducts (mp 172–173° and 214–215°) which differ only in the stereochemistry of the chlorine atoms.[3]

The stereochemistry of the 17′ chlorines have been assigned[3] as being endo in the higher melting isomer **5** and exo in the other (**6**) on the basis of the observed long-range coupling (J = 1.5 Hz, see Table I) between

TABLE I

SUMMARY OF NMR DATA OF DICHLOROETHYLENE ADDUCTS **5** AND **6**

Compd	Resonances ($CDCl_3$; δ, ppm) 18-H	21-H	16′-H	17′-H	H–H spin couplings,[a] Hz
5, R = $COCH_3$	0.61	2.18	3.80	4.34	$J_{16\beta,16'\alpha}$ = 4.5
					$J_{16\beta,17'\beta}$ = 1.5
					$J_{16'\alpha,17'\beta}$ = 6.0
6, R = $COCH_3$	0.71	2.26	4.42	4.26	$J_{16\beta,16'\beta}$ = 9.5
					$J_{16\beta,17'\alpha}$ = 0
					$J_{16'\beta,17'\alpha}$ = 7.5

[a] Confirmed by double resonance experiments.

the 16β and 17′β protons in **5** which are in a "W" spatial relationship to each other. This long-range coupling is absent in **6**. Since the configuration at the 16′ position could not be assigned with confidence on the basis of the $J_{16\beta,16'}$ and $J_{16',17'}$ values alone, the 3β-bromoacetate derivative of isomer **5** was subjected to X-ray analysis ($C_{25}H_{33}O_3Cl_2Br$; orthorhombic crystals with a = 32.37, b = 9.77, and c = 7.89 Å; space group $P2_12_12_1$ from systematic absences[8]), establishing the presence of a 16′ exo chlorine in **5**. The cyclobutyl ring in **5** is planar to within 0.015 Å with 110 and 119° dihedral angles between the 16β,16′α and 16′α,17′β protons.

The stereochemistry of the 16′ chlorine in **6** can now be inferred by comparison of the $J_{16\beta H,16'H}$ (9.5 *vs.* 4.5 Hz) and $J_{16'H,17'H}$ values (7.5 *vs.* 6.0 Hz) in the two isomers (see Table I). These values indicate a difference in the relative configuration of the 16β,16′ protons which is trans in compound **5** and therefore has to be cis with a very small dihedral angle in **6**. Consequently, the configuration of the 16′ chlorine is endo in **6** which is consistent with the observed trans relationship of the 16′,17′ protons in both isomers.

The fact that both *cis*- and *trans*-dichloroethylene gave the same product composition[3] is in good agreement with a stepwise addition mechanism forming a diradical intermediate[7] which can undergo free rotation at the 16′–17′ bond before ring closure.

Experimental Section[9]

3β-(*p*-Bromobenzoyloxy)androst-5-eno[16α,17-*d*]-2′,2′,3′,3′-tetrafluoro-2′,3′-dihydro-6-methylpyran (4, R = COC_6H_4Br).—A solution of the 3β-acetoxy compound[3] **4** (R = $COCH_3$, 450 mg) in methanol (30 ml) containing potassium bicarbonate (450 mg) and water (0.6 ml) was heated under reflux for 1.75 hr. After cooling, the methanol was removed under reduced pressure and the residue extracted with ethyl acetate. Drying (Na_2SO_4) and evaporation of the solvent gave the crude crystalline 3β-hydroxy compound **4** (R = H, 380 mg) which was dissolved in pyridine (5 ml) and heated for 2 hr on a steam bath with *p*-bromobenzoyl chloride (420 mg). The reaction mixture was poured into water and extracted with ethyl acetate. The extract was washed with dilute hydrochloric acid and with aqueous sodium carbonate. Drying and evaporation of the solvent yielded the crude *p*-bromobenzoate **4** (R = *p*-COC_6H_4Br, 510 mg). Recrystallization from chloroform–methanol gave the analytical sample: mp 254–256°; ν_{max} (Nujol) 1720 cm^{-1}; nmr ($CDCl_3$) 0.96 (18-H), 1.07 (19-H), 1.89 (d, $J_{16\beta H,21H}$ = 2 Hz, 21-H), 3.26 (b m, 16β-H), 4.6–5.0 (3α-H), 5.42 (m, $W_{1/2}$ = 9 Hz, 6-H), 7.56 (d, J = 8.5 Hz, aromatic H), and 7.89 ppm (d, J = 8.5 Hz, aromatic H); mass spectrum 596 and 598 (M^+ with ^{79}Br and ^{81}Br), 396 ($M^+ - BrC_4H_6COOH$). *Anal.* Calcd for $C_{30}H_{33}O_3F_4Br$: C, 60.31; H, 5.52. Found: C, 60.44; H, 5.77.

3β-Hydroxy-16α,17α-(16′-*exo*,17′-*endo*-dichloro)ethylenepregn-5-en-20-one (5, R = H).—A solution of 3β-acetoxy-16α,17α-(16′-*exo*,17′-*endo*-dichloro)ethylenepregn-5-en-20-one[3] (**5**, R = $COCH_3$, 2.5 g) in tetrahydrofuran (80 ml) was treated with 1.5% methanolic potassium hydroxide (250 ml) at room temperature for 1.5 hr. The reaction mixture was diluted with water and extracted with methylene chloride, and the organic extracts were washed with water and then dried (Na_2SO_4). Evaporation of the solvent and recrystallization of the residue from acetone gave the 3β-alcohol (**5**, R = H, 2.0 g): mp 224–226°; $[\alpha]D$ −81°; $\lambda_{max}^{dioxane}$ 286–290 nm (ϵ 81); ν_{max} 3550, 3400, 1706, 1670, 796,

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(6) W. L. Dilling, T. E. Tabor, F. P. Boer, and P. P. North, *J. Amer. Chem. Soc.*, **92**, 1399 (1970).

(7) The possibility of this intermediate being a zwitterion is not excluded.

(8) Full details of the X-ray work will be published in *Acta Crystallogr.*

(9) The X-ray diffraction intensities were measured on a Picker diffractometer with full circle goniostat, using Cu radiation. The structures were solved by the heavy atom method. For compound **5**, R = $COCH_2Br$, the positional and anisotropic temperature parameters were refined by block-diagonal least squares to a final reliability factor of 6.9%; the refinement was based on 1991 reflections. The experimental details of the X-ray work on the 3β-(*p*-bromobenzoate) of compound **4** are described in ref 4. The nmr spectra were measured by Mr. John Murphy and Mrs. Janis Nelson on a Varian HA-100 spectrometer using tetramethylsilane as internal reference. The mass spectra were recorded by Mr. John Smith on an Atlas CH-4 spectrometer equipped with an EFO-4B ion source at 70-eV ionizing potential.

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.

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

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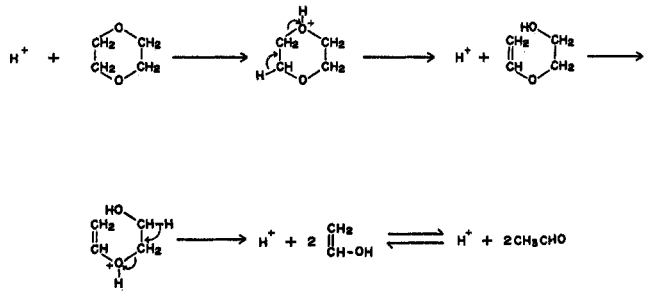
The use of hydrogen chloride in anhydrous dioxane as a catalyst for the conversion of ribonucleosides to corresponding 2′,3′-*O*-alkylidene derivatives has been described by Chládek.[2-4] It has now been found that this catalyst–solvent system, when employed in combination with acetonitrile,[5] effects 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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(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.

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