The n.m.r. δ 7.0 (m, 8H) aromatic and 6.6 (s, 4) vinyl is consistent with the structure of 1, and identical with that previously reported (4).

7-Methylenedibenzo[a,e]cycloheptatriene (2)

Samples were prepared by two methods: (a) by refluxing 1 with an excess of p-toluenesulfonic acid hydrate in benzene followed by refluxing the tosylate with sodium hydroxide – ethanol,³ and (b) by reacting dibenzo[a,e]cycloheptatrienone with methylmagnesium iodide followed by dehydration (2). After recrystallization from aqueous ethanol, the respective samples proved identical, m.p. 117–118° (lit. (6) 118–119°). The i.r. showed major absorptions at 11.0, 12.3, 12.5, and 12.9 μ , and was identical with that published by Cope (2), incorrectly indicated as 1. The n.m.r. δ 7.35 (m, 8H) aromatic, 6.82 (s, 2) vinyl, and 5.25 (s, 2) *exo*-vinyl is quite consistent with the structure of **2**.

³Essentially the procedure of Bucur *et al.* (6).

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Thermal Rearrangement of Acyl Groups in Anhydronucleosides. A Convenient Synthesis of 5'-O-Acetylanhydrouridine¹

NOTES

K. K. OGILVIE, J. B. WESTMORE, G. TAYLOR, D. LIN, D. IWACHA,² H. WAYBORN, AND G. E. DUNN

Department of Chemistry, University of Manitoba, Winnipeg, Manitoba

Received March 8, 1972

The mass spectra of acylanhydronucleosides suggested that the acyl groups undergo a thermal rearrangement. This was confirmed by studying the melting profiles of these compounds in a differential scanning calorimeter. The results have led to a convenient synthesis of 5'-acetylanhydrouridine.

Les spectres de masse des acylanhydronucléosides laissent penser que les groupes acyle subissent un réarrangement thermique. Ceci a été confirmé par l'étude des profils de fusion de ces composés, dans un calorimètre à balayage différentiel. Les résultats ont conduit à une synthèse commode de l'acétyl-5' anhydrouridine.

Canadian Journal of Chemistry, 50, 2365 (1972)

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We have recently developed a method for incorporating 2'-anhydronucleosides into nucleotide chains (1). To permit maximum flexibility in this approach we needed acid- and baselabile protecting groups for both the 3'- and 5'positions. Further, these groups should be sufficiently labile to be removed without opening the anhydro-ring, yet stable during phosphorylation procedures. The monomethoxytrityl (MTr—) and the acetyl (—Ac) groups satisfy these requirements for acid- and base-labile protecting groups respectively. Schemes 1 and 2 (to be discussed later) illustrate the methods by which 3'- and 5'-O-acetyl derivatives can be prepared. These multistep procedures are required because acetylating reagents generally have little preference for reaction at the 5'position vs. the 3'-position. 5'-Derivatives in particular are not easy to prepare in high overall yield in just a few reaction steps. For example 5'-O-acetylanhydrouridine has been prepared by Todd and co-workers (2) and Verheyden and Moffat (3) both using the same five-step synthesis from uridine giving an overall yield of about 25%. We wish to report a simple synthesis of 5'-O-acetyl-2,2'-anhydro-1- β -D-arabinofuranosyluracil (5'-AcAU, 6) by a method suggested from our mass spectral investigations of 3',5'-di-O-acetyl-2,2'-anhydro-1-β-D-arabino-

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¹Part VII in a series on anhydronucleosides. ²NRCC Scholarship holder 1968-1972.



furanosyluracil (DiAcAU, 5) and 3'-O-acetyl-2,2'-anhydro- $1-\beta$ -D-arabinofuranosyluracil (3'-AcAU, 4).

As part of our investigation of anhydronucleosides we have been carrying out a systematic study of their mass spectra. A sample of 3'-AcAU was prepared by the route shown in Scheme 1. Monomethoxytrityl chloride (MTrCl) reacts with 2,2'-anhydro-1- β -D-arabinofuranosyluracil (AU, 1) in pyridine to produce 5'-Omonomethoxytritylanhydrouridine (2) in 60% yield. Acetylation of 2 to produce 3 followed by detritylation using acetic acid at room temperature yields 4.

In the course of the mass spectral studies we noticed that the mass spectra obtained when 4 and 5 were introduced into the mass spectrometer were similar. In particular, the mass spectrum obtained when 4 had been placed in the mass spectrometer sample probe showed a peak at m/e 310 (mw of 5 is 310) as well as at m/e 268 (mw of 4) and at 226 (mw of 1). Samples of 4 were carefully analyzed by paper chromatography before they were introduced into the mass spectrometer. No diacetylanhydrouridine or anhydrouridine could be detected in these

samples under conditions where less than 1% could be detected. However, when the unvaporized residues were removed from the mass spectrometer sample probe (after the spectrum had been recorded) and analyzed by paper chromatography they were always found to contain 1, 4, 5, and a material moving slightly faster (solvent A) than 4. This unidentified material had an u.v. spectrum characteristic of anhydrouridines and was suspected to be 5'-O-acetyl-2,2'-anhydro-1- β -D-arabinofurano-syluracil (6).

We synthesized 6 by an alternate route (Scheme 2) for comparison with our unidentified derivative. 5'-Acetyluridine (4) was treated with diphenyl carbonate in dimethylformamide (5) to give 6. Compounds 1 and 5 were also detected among the products but no 4 was observed. The yield of 6 from this reaction was 45%. We found the synthetic 6 to be identical to our unidentified material from the residue recovered from the mass spectrometer when 4 had been inserted into the sample probe.

The mass spectrum of **6** was similar to that of **4** showing again major peaks at m/e 310, 268, and 226. The relative peak heights differed in

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SCHEME 2

TABLE 1. Analysis of mass spectral residues and DMF reaction products (%)

Starting material:	3'-AcAU		5'-AcAU		
-	Residue from		Residue from		
Product composition	Mass spectros- copy	DMF reaction	Mass spectros- copy	DMF reaction	
DiAcAU	6.6	16	14	6	
5'-AcAU	2.6	13	58	69	
3'-AcAU	84.2	50	5	0	
AU	6.6	21	23	25	

the two cases. The paper chromatographic analyses of the residues recovered from the sample probe are shown in Table 2. Similar mass spectral results were obtained when samples were studied with a Finnigan 1015 quadrupole mass spectrometer.

The mass spectrometric results are not an artifact of electron impact but are evidently thermal in origin. The thermal rearrangement of the anhydro-derivatives was studied further in a differential scanning calorimeter (Perkin-Elmer DSC-1B). Samples of 4 were heated from room temperature to 260 °C at 10°/min in specially designed glass containers (6) sealed at reduced pressure. The results of paper chromatographic analyses are shown in Table 1. These results clearly show that the rearrangement was affected only slightly by reduction in pressure (at atmospheric pressure a small amount of decomposition to a material having a uracil-like u.v. spectrum occurred). The rearrangement was also independent of whether a glass or aluminum sample holder was used. Subsequent experiments were carried out in aluminum pans at atmospheric pressure.

Tables 1 and 2 show that compound 6 undergoes a thermal rearrangement to produce the same kind of products obtained from 4. The presence of diacetylanhydrouridine in the products clearly indicated that some intermolecular transesterification had occurred. As

TABLE 2. Thermal rearrangement of acetylated anhydrouridines in the DSC

			Temperature	Product composition (%)				
Sample container	Starting material	Pressure	reached (°C)	DiRAU	5'-RAU	3'-RAU	AU	U
GP*	3'-AcAU	10^{-6} mm	260	23	35	20	22	
GP	3'-AcAU	10^{-3} mm	260	22	32	22	24	
AP†	3'-AcAU	1 atm	260	24	24	28	22	2
GP	3'-AcAU	l atm	260	22	20	34	22	2
AP	5'-AcAU	1 atm	210	12	57	4	2 7	
AP	DiAcAU + AU							
	(1:1.15)	1 atm	260	19	37	10	25	9
AP	3'-PvAU	1 atm	270	23	\sim	\sim	21	5
					5	1		
AP	DiPvAU + AU							
	(1:1.7)	l atm	270	14	4	0	40	6

*GP = glass pan (6). \uparrow AP = aluminum pan.

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a result a mixture of 5 and 1 was heated to 260 °C under controlled conditions in the DSC. The presence of 6 as the major product (Table 2) was encouraging. There was also a significant amount (9%) of decomposition to material having a uracil-like u.v. spectrum (this could result from cleavage of either the anhydro or both the anhydro and glycosidic bonds to give uracil derivatives).

To test the utility of the method as a source of 6 on a preparative scale, 100 mg of a mixture of 5 and 1 (1:1.15 mol ratio) was placed in a small test tube which was suspended in an oil bath maintained at 260 °C (this temperature would ensure rapid melting of the mixture). Complete melting occurred in 55 s and the sample was cooled rapidly to room temperature. The products, isolated by chromatography, contained 6 and 4 in 51 and 12% yields (crystallized from methanol) respectively. Since the monoacetyl derivatives have very similar properties, a combination of thick-layer and paper chromatography was required to separate them. This difficulty is easily avoided by heating the mixtures in the melt for slightly longer periods of time. This results in exclusive formation of the 5'-isomer $\mathbf{6}$ which is readily isolated and in higher yields by thick-layer chromatography in tetrahydrofuran. The reaction is easily carried out on larger scales in the same manner. The method of heating is not critical and for our own purposes the sample is kept in the melt for 2-3 min using a gas-burner for heat and in all cases only the 5'-isomer is obtained. This represents an exceedingly simple synthesis of **6** from readily available materials.

In the preparative reaction some decomposition had occurred to yield products having a uracil-like spectrum. These products were very numerous and only uracil was positively identified. Most of the other products were probably acetylated uridines or arabinouridines. Samples maintained at 260 °C for longer periods of time gave greater amounts of decomposition products. Uracil was the only identifiable product from a reaction mixture held at 260 °C for 15 min.

In order to check on the generality of this rearrangement, samples of 3'-O-pivaloylanhydrouridine (PvAU) and a mixture of 3',5'-di-O-pivaloylanhydrouridine (DiPvAU) and anhydrouridine were heated in the DSC from room temperature to 270 °C at 10° /min. The results, shown in Table 2, confirm that rearrangement had occurred. We have been unable to separate mixtures of 3'-PvAU and 5'-PvAU and as a result only the sum of the two is shown in Table 2.

A similar thermal transfer of acetyl groups in nucleoside derivatives using a fusion method has been described by Michelson *et al.* (7). In their case acetyl groups migrated among secondary hydroxyl groups in protected adenosine derivatives. In our case the migration occurs between secondary and primary hydroxyls with the product being the more stable primary ester.

We also heated samples of 4 and 6 individually in dimethylformamide solutions held at 150 °C and found that rearrangement also occurred in solution. These results are shown in Table 1.

This study has produced a very useful route to 5'-O-acetylanhydrouridine. However, it also points out the necessity of exercising care when interpreting the mass spectra of semiesterified molecules of low volatility.

Experimental

General Methods

Thin-layer chromatography was carried out on Eastman Chromagram Sheets 6060 by the ascending technique, Thick-layer chromatography was carried out on glass plates $(20 \times 20 \text{ cm})$ coated with a 2 mm thick layer of silica gel DSF-5 (Mondray Chemicals Ltd.). Paper chromatography was carried out on Whatman 3MM paper by the descending technique. The solvent system employed in paper chromatography was solvent A; n-butanol:ethanol:water (4:1:5, v/v/v), the organic phase was used. Nucleosides and their derivatives were detected on paper chromatograms, thinand thick-layer plates, using an u.v. source (Mineralite, output $\simeq 254$ nm). Nucleosides were eluted from the paper chromatograms, diluted to volume and their absorbances recorded in the u.v. on a Cary 14 spectrophotometer. The term o.d. unit (8) refers to the extinction of a solution of a nucleoside at neutral pH in 1 ml of solution using a 1 cm light path quartz cell.

The i.r. spectra were obtained on a Perkin-Elmer 337 recording instrument using KBr disks for sample preparation. Melting points were determined on a Fisher-Johns melting point apparatus and are reported uncorrected. Elemental analyses were performed by Galbraith Labs, Knoxville, Tennessee.

Mass Spectra

Mass spectra were recorded by a Perkin-Elmer Hitachi RMU-6D single-focusing instrument. Samples were introduced to the mass spectrometer in a solid sample probe via a vacuum lock. The electron energy was 50 V. After preliminary experiments the following procedure was used. The

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Can. J. Chem. Downloaded from www.nrcresearchpress.com by 198.178.132.247 on 11/14/14 For personal use only. ionization chamber temperature and sample heater block were each maintained at 135 °C. The sample probe was inserted into the heater block and spectra were recorded as soon as vaporization started to occur. After the spectra were recorded (total time 15 min) the remains of the samples were withdrawn from the instrument and analyzed by paper chromatography. Results of these experiments are shown in Table 1. Clearly 1, 4, 5, and 6 were obtained when starting with pure samples of either 4 or 6.

Calorimetric Studies

Can. J. Chem. Downloaded from www.nrcresearchpress.com by 198.178.132.247 on 11/14/14 For personal use only. Samples were heated through the melting endotherm (6) in a differential scanning calorimeter (Perkin-Elmer DSC-1B). Typical samples of 2-10 mg and a heating rate of 10°/min were used. After melting, the samples were removed, cooled to room temperature, and analyzed by paper chromatography in solvent A. The results are shown in Table 2. In some cases a product moving slightly faster than DiAcAU (solvent A) was observed. The u.v. spectrum (water) of this material was similar in form to that of uracil with λ_{max} at 260 nm (this compound was most likely an acetylated uridine or arabinouridine resulting from some decomposition of the anhydro-structure).

3'-O-Pivaloyl-2,2'-anhydrouridine, 5'-O-pivaloyl-2,2'-anhydrouridine, and 3',5'-di-O-pivaloyl-2,2'-anhydrouridine were prepared as described by Wayborn (9). 2,2'-Anhydrouridine was prepared by the method of Hampton and Nichol (5).

5'-O-Monomethoxytrityl-2,2'-anhydrouridine (MTrAU, 2)

Anhydrouridine (4.35 g, 19.2 mmol) and monomethoxytrityl chloride (6 g, 19.5 mmol) were stirred in dry pyridine (100 ml) for 4 days. The solvent was removed at reduced pressure and the residue was dissolved in a mixture (300 ml) of chloroform and water (1:1). The chloroform layer was separated and concentrated to a small volume. White crystals of MTrAU separated and were collected by filtration (5.7 g, 60%), m.p. 154–158 °C. Principal bands in the i.r. spectrum occurred at 6.07, 6.13, 8.05, and 14.2 μ .

Anal. Calcd. for $C_{29}H_{26}O_6N_2$: C, 69.87; H, 5.26; N, 5.62. Found: C, 70.23; H, 5.28; N, 5.53.

5'-O-Monomethoxytrityl-3'-O-acetyl-2,2'-anhydrouridine (MTrAU-Ac, 3)

MTrAU (2, 2.5 g, 5 mmol) and acetic anhydride (0.8 ml) were stirred in dry pyridine (15 ml) for 12 h. The solution was poured into ice water (500 ml) and the precipitate was collected, dissolved in chloroform, and dried over sodium sulfate. The chloroform solution was concentrated to a small volume and on addition of hexane a white precipitate formed which was collected by filtration and dried to yield 2.6 g (95%) of MTrAU-Ac (3, m.p. 100–107 °C). Principal bands in the i.r. spectrum occurred at 5.7, 6.1, 12.1, 13.3, and 14.2 μ . The u.v. spectrum in ethanol showed λ_{max} of 230 (ϵ 19 000) and λ_{min} of 223 nm (18 300).

Anal. Calcd. for $C_{31}H_{28}N_2O_7$: C, 68.88; H, 5.22; N, 5.18. Found: C, 68.78; H, 5.14; N, 5.08.

3'-O-Acetyl-2,2'-anhydrouridine (3'-AcAU, 4)

MTrAU-Ac (3, 2.2 g, 4 mmol) was dissolved in 80% acetic acid (25 ml) and stirred at room temperature for 3 h. The solvents were removed at reduced pressure and the residue was washed with ether and crystallized from ethanol (0.7 g, 66%), m.p. 204-209 °C. The i.r. spectrum showed

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TABLE 3. Physical properties of anhydronucleosides

Compound	m.p. (°C)	λ _{max} , (nm)*	$R_{\rm f}({\rm A})^{\dagger}$	<i>R</i> _f THF
AU	244-248	249	0.30	0.05
3'-AcAU	204-209	249	0.46	0.11
5'-AcAU	164-167	249	0.51	0.16
DiAcAU	186-187	249	0.60	0.23
3'-PvAU	240242	249	0.75	0.23
5'-PvAU	210-215	249	0.75	0.23
DiPvAU	227-231	249	0.87	0.47
DiAcAU 3'-PvAU 5'-PvAU DiPvAU	186–187 240–242 210–215 227–231	249 249 249 249 249	0.60 0.75 0.75 0.87	0.23 0.23 0.23 0.47

*Both water and ethanol used as solvents in all cases. †Solvent A experimental section.

principal bands at 5.8, 5.99, 8.2, and 13.1 μ . The u.v. spectrum in ethanol showed λ_{max} 249 (ε 8220), 224 (9600), and λ_{min} 237 nm (ε 7330).

Anal. Calcd. for $C_{11}H_{12}N_2O_6$: C, 49.25; H, 4.51; N, 10.44. Found: C, 49.10; H, 4.50; N, 10.26.

5'-O-Acetyl-2,2'-anhydro-1-β-D-arabinofuranosyluracil (5'-AcAU, 6)

(A) 5'-Acetyluridine ((4), 140 mg, 0.5 mmol), diphenyl carbonate (140 mg), and sodium bicarbonate (12 mg) were added to DMF (0.5 ml) and the mixture was heated at 150 °C for 30 min. The solution was cooled to room temperature and applied to two t.l.c. plates which were developed first in ethyl acetate and then three times in tetra-hydrofuran. Three anhydronucleoside bands were apparent including diacetylanhydrouridine, anhydrouridine, and a product moving between these two. This latter product was isolated and identified as 5'-AcAU (60 mg, 45%) with m.p. 164-167 °C (lit. m.p. 166-167 °C (2)). $R_{\rm f}$ values are shown in Table 3.

(B) One hundred milligrams of a mixture of DiAcAU and AU (1:1.15, molar ratio) was placed in a small test tube suspended in an oil bath maintained at 260 °C. As soon as the mixture had completely melted (55 s) the sample was removed, cooled to room temperature, and applied to a thick-layer plate which was developed first in tetrahydro-furan (THF). Two nucleoside bands moved up the plate in THF ($R_{\rm f}$ 0.5, 0.7) and were eluted. Both of these bands contained numerous products (paper chromatography solvent A) all of which had $\lambda_{\rm max}$ (H₂O) 260 and $\lambda_{\rm min}$ (H₂O) 231 nm. The total weight of material from the two bands was 20 mg and the only compound positively identified was uracil (4 mg).

The original thick-layer plate was developed in ethanol and another nucleoside band was obtained. This band was eluted and re-applied to another thick-layer plate which was developed five times in THF. Four bands separated with DiAcAU (8 mg, 0.026 mmol) moving fastest and AU (16 mg, 0.071 mmol) moving slowest. In between these were two bands moving very close together. The fastest band contained only 5'-AcAU while the slower band contained a mixture of 5'-AcAU and 3'-AcAU. This mixture was applied to Whatman 3MM paper developed in solvent A and the two materials separated cleanly. The yield of 3'-AcAU was 11 mg (0.041 mmol, 12%) while the total yield of 5'-AcAU (crystallized from ethanol) was 48 mg (0.18 mmol, 51% based on the total mmoles of acetyl groups in the starting materials, m.p. 165-167 °C).

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(C) A mixture containing 62 mg of DiAcAU and 51 mg of AU was heated as above at 260 °C for 2.5 min. The product was dissolved in ethanol and applied to a single thick-layer plate which was developed four times in THF. Behind the decomposition products (at the solvent front) were three cleanly separated bands which were eluted with ethanol and identified as DiAcAU (3 mg), 5'-AcAU (75 mg, 70%), and AU (10 mg).

When this experiment was repeated, except that the sample was held at 260 °C for longer periods of time, the amount of decomposition increased markedly. In one reaction held at 260 °C for 15 min the only identifiable u.v. absorbing material was uracil.

(D) A mixture containing 620 mg of DiAcAU and 504 mg of AU was heated at 260 °C in a 100 ml round-bottom flask for 3 min and cooled to room temperature. The product was dissolved in ethanol and applied to eight thick-layer plates developed as in section C above. The yield of 5'-AcAU from this reaction was 720 mg (67%). The same result was obtained when the mixture was melted using a gas-burner for heat (total time in the melt 2-3 min).

Thermal Rearrangement of Acetyl Groups in Dimethylformamide (DMF)

Samples of 4 and 6 were heated separately in DMF at $150 \,^{\circ}C$ for 30 min. The solutions were cooled to room

temperature and applied to Whatman 3MM paper developed in solvent A. The results are shown in Table 1.

We wish to acknowledge financial support from the National Research Council of Canada.

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A Nuclear Magnetic Resonance Study of the Symmetry of the Proton Spins in Ethylene Sulfite in a Nematic Solvent¹

M. A. RAZA AND L. W. REEVES

The Chemistry Department, University of Waterloo, Waterloo, Ontario

Received February 10, 1972

The proton magnetic resonance spectrum of ethylene sulfite dissolved in the nematic phase N(p-methoxybenzylidene)-p-n-butylaniline has been recorded and analyzed. The dipole-dipole coupling constants derived show that the four protons are arranged in an effective plane with C_{2v} symmetry. The spectrum is deceptively similar to that expected for D_{2h} symmetry but errors between the experimental and the optimized computed spectrum are unacceptably large with this assumption. The two vicinal protons *cis* to the extra ring oxygen are closer together than the two *trans* vicinal protons. A comparison is made with the molecule ethylene carbonate studied previously in the same nematic solvent.

Le spectre de résonance magnétique nucléaire du sulfite d'éthylène dissout en phase nématique N(p-méthoxybenzylidène) p-n-butylaniline a été enregistré et analysé. Les constantes de couplage dipôle-dipôle montrent que les quatre protons sont dans un arrangement effectif plan selon la symétrie C_{2v} . Le spectre est d'une similitude "décevante" à celui attendu pour la symétrie D_{2h} mais les écarts entre les spectres expérimental et calculé sont trop grands pour retenir une telle hypothèse. Les deux protons vicinaux en *cis* par rapport à l'oxygène sont plus rapprochés que les deux protons vicinaux *trans*. Une comparaison est faite avec la molécule de carbonate d'éthylène précédemment étudiée, dans le même solvant nématique.

Canadian Journal of Chemistry, 50, 2370 (1972)

Introduction

We have recently reported comparative studies of the proton magnetic resonance (n.m.r.) spectra

¹Research supported by operating grants provided by the Defence Research Board and the National Research Council of Canada. of a series of ring compounds with four spins dissolved in both lyotropic and thermotropic nematic phases (1-4). Ethylene carbonate (EC) and ethylene monothiocarbonate (EMTC) do not have the same geometry in the two types of nematic phase. Ring puckering motions which

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