Table 1. Polymerization of 4-Hydroxy-4-phenyl-1,6-heptadiyne by Various Catalyst System[a]

Exp. No.	Catalyst System (:) mole ratio[b]	Polymer Yield (%)
1	$MoCl_5$	98
2	$MoCl_5$ (n-Bu)$_4$Sn (1 : 2)	85
3	$MoCl_5$ $EtAlCl_2$ (1 : 2)	76
4	WCl_6	0
5	WCl_6 (n-Bu)$_4$Sn (1 : 2)	0
6	WCl_6 $EtAlCl_2$ (1 : 2)	5

[a]Polymerization was carried out in dioxane at 60℃ for 24 hrs. Initial monomer concentration [M_o] was 1.0 M and monomer to catalyst mole ratio was 50. [b]Mixture of catalyst and cocatalyst was aged at 30℃ for 15 min before use.

are soluble and relatively stable in air has been intensively investigated.[2] Since various substituted acetylenes have been polymerized to conjugated polymers by transition metal catalysts, the cyclopolymerizations of nonconjugated diynes were investigated in an attempt to prepare a polymer that would containing alternating double bond and single bonds along the polymer backbone and a cyclic recurring unit.[3] We reported that 1,6-heptadiyne derivatives were cyclopolymerized by transition metal catalysts.[4-7] However, it has been known that the acetylenic monomers containing hydroxy functional group were hardly polymerized by transition metal catalysts. Recently, we found that Mo-based catalysts polymerized dipropargylcarbinol(4-hydroxy-1,6-heptadiyn) containing hydroxy functional group.[8] However, the molecular weight of poly(4-hydroxy-1,6-heptadiyne) was barely several thousand and the properties had depreciated.

The present communication reports the study on the cyclopolymerization of 4-hydroxy-4-phenyl-1,6-heptadiyne (HPH) containing hydroxy group and phenyl substituent at 4-position.

All the procedures of the preparation of catalysts, and polymerization were carried out under dry nitrogen atmosphere.[5]

Table 1 shows the results of the polymerization of 4-hydroxy-4-phenyl-1,6-heptadiyne by various catalysts. The $MoCl_5$ -based catalysts have all effective catalytic activity. However, poly(HPH) is hardly obtained by using WCl_6-based catalysts. It seems that functional hydroxy group in monomer inhibits catalytic activity of WCl_6, though hydroxy group is considerably hindered by bulky phenyl substituent. (n-Bu)$_4$Sn and $EtAlCl_2$ have been known to be an excellent cocatalyst for the polymerization of mono- and di- substituted acetylenes.[9,10] However, neither (n-Bu)$_4$Sn nor $EtAlCl_2$ have any effect as a cocatalyst of $MoCl_5$ and WCl_6 on the cyclopolymerization of HPH. HPH is effectively polymerized by $MoCl_5$ alone.

The obtained highly colored (red black) poly(HPH) is completely soluble in common organic solvents. The ^{13}C-NMR spectrum of poly(HPH) shows the chemical shifts at 130 and 140 ppm due to the polyconjugated olefinic carbon. The IR spectrum also shows the conjugated carbon-carbon double bond stretching at 1600-1650 cm^{-1}. In the UV-visible spectrum of poly (HPH), a characteristic peak of conjugated polymers, broad $\pi-\pi^*$ absorption, appears at visible region (300-700 nm) with maximum 500 nm.

In the above spectroscopy data and solubility behavior, we suggest that poly(HPH) possesses polyene structure having cyclic recurring units in the polymer backbone.

The number average molecular weights ($\overline{Mn}$) of poly (HPH) are in the range of 20000-30000, although that of poly(4-hydroxy-1,6-heptadiyne) only reaches several thousand.

More detailed studies on the cyclopolymerization of 1,6-heptadiyne derivatives containing hydroxy group and various substituents by transition metal catalysts and the physcial properties of resulting polymers are in progress.

Acknowledgement. The financial supports of the Korea Science & Engineering foundation and the Ministry of Education, Korea are gratefully appreciated.

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Preparation and Reaction of Carbohydrate Cyclic Sulfates: Efficient Synthesis of O^2,2'-Cyclopyrimidine Nucleoside and Ara-U

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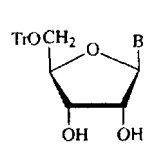
Cyclopyrimidine nucleosides have been served as valuable models for physicochemical studies on the base-sugar con-

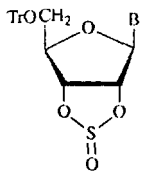
formations and have been useful intermediates for chemical modification of base and sugar moieties in natural nucleosides.[1] Various important nucleosides including 1-β-D-arabinofuranosyluracil(ara-U) are readily prepared from O^2,2′-cyclopyrimidine nucleosides. The O^2,2′-cyclopyrimidine nucleoside was initially prepared from 3′,5′-di-*O*-acetyl-2′-tosyluridine by treatment with methanolic ammonia.[2] Since the development of the more direct synthesis of the O^2,2′-cyclopyrimidine nucleoside from 5′-*O*-trityluridine with diphenyl thiocarbonate by Fox *et al.*,[3] a variety of other efficient reagents for the cyclopyrimidine nucleoside formation have been introduced. These include α-acetoxyisobutyryl chloride,[4] phosphoryl chloride,[5] diethyl azodicarboxylate with triphenylphosphine,[6] N-bromosuccinimide,[7] and triphenylmethyl tetrafluoroborate.[8]

Herein we report the preparation of carbohydrate cyclic sulfates and sulfites and the conversion of the cyclic sulfite into a O^2,2′-cyclopyrimidine nucleoside and ara-U. Preparation of the cyclic sulfates and sulfites and their reactions with nucleophiles have been known for a long time, especially in carbohydrate chemistry.[9] Recent works by Sharpless *et al.*, have provided an easier access to cyclic sulfates and showed their usefulness in organic synthesis.[10]

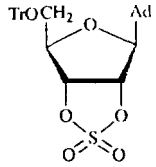
5′-*O*-Tritylladenosine 2′,3′-cyclic sulfite(**3**)[11] was prepared from 5′-*O*-trityladenosine(**1**) in 94% yield using thionyl chloride in pyridine. Because of the generation of a new chiral center at sulfur, the ^{1}H-NMR spectrum of cyclic sulfite **3** showed the signals corresponding to a mixture of two diastereomers. However, the diastereomeric mixture could not be separated on TLC or by a column chromatography. Cyclic sulfite **3** was then oxidized to 5′-*O*-tritylladenosine 2′,3′-cyclic sulfate(**4**)[12] in 93% yield employing $RuCl_3$ and $NaIO_4$ in CCl_4 /CH_3CN/H_2O solvent as described by Sharpless.[10] Similary, 5′-*O*-trityluridine 2′,3′-cyclic sulfite(**5**)[13] was readily prepared from 5′-*O*-trityluridine(**2**) in 97% yield. Cyclic sulfite **5**, however, was not oxidized to the corresponding sulfate with $RuCl_3$-$NaIO_4$ or with other oxidizing agents. Direct cyclic sulfation of **2** with sulfuryl chloride was also not fruitful. The difficulty in the preparation of the 2′,3′-cyclic sulfate of uridine might be due to its higher ring strain energy than that of the 2′,3′-cyclic sulfate of adenosine or other 1,2-cyclic sulfates.[14]



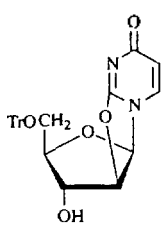
1 B = Ad
2 B = Ur



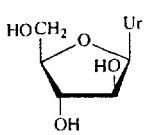
3 B = Ad
5 B = Ur



4



6



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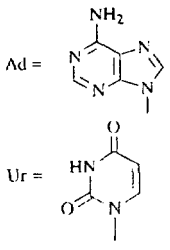

Cyclic sulfite **5** was readily transformed into cyclopyrimidine nucleoside **6** by treatment with a base. To a solution of cyclic sulfite **5** (250 mg, 0.46 mmol) in 50% aqueous ethanol (16 m*l*) was added 1.0 N NaOH(0.47 m*l*) and the solution was stirred at 45-50℃ for 1 hr. The reaction mixture was partitioned between ether and water. The organic phase was washed with 0.1 N sodium bicarbonate, dried over magnesium sulfate, and evaporated *in vacuo* to afford pure 5′-*O*-trityl-O^2,2′-cyclouricine(**6**)[15] in 98% yield. Acid hydrolysis of compound **6** by the known procedure[2] affored ara-U(**7**)[16] in 70% yield.

The present method for the synthesis of the O^2,2′-cyclopyrimidine nucleoside is superior to the previously known methods[3-8] in a few aspects. The reaction proceeds so cleanly that the usual work up affords pure products, **5** and **6**. The overall yield of **6** in the present method is 95% from **3** and 92% from uridine. The usual yields reported in other methods ranges from 35% to 72% except the method of Furukawa and Honjo.[5] Although Furukawa and Honjo obtained 3′,5′-di-*O*-acetyl-O^2,2′-cyclouridine from uridine in 94% yield, the product they obtained is protected both at 3′- and 5′-positions with same acetyl groups and thus the selective elaboration of 3′-and 5′-positions would require extra steps.

On the other hand, the azidonation of **4** with sodium azide gave a mixture of 2′- and 3′-azidonucleosides but the regioselectivity was not observed. Reduction of **4** with various hydride reducing agents was also not regioselective.

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11. Compound **3**, a mixture of two diastereomers : TLC(SiO_2, 9 : 1 ethyl acetate/methanol) R_f=0.57; IR 1208 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 3.38 (d), 4.48 (dd), 4.9 (dd), 5.58 (s), 5.69 (dd), 5.92 (dd), 6.12 (d), 6.28 (d), 6.13 (d), 6.44 (d), 7.21-7.41 (m), 7.88 (s), 7.98 (s), 8.10 (s), 8.16 (s).
12. Compound **4** : TLC(SiO_2, 9 : 1 ethyl acetate/methanol) R_f=0.64; IR 1212, 1400 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 3.38 (d, 2H), 4.65 (dd, 1H), 5.61 (brs, 2H), 5.81 (dd, 1H), 6.23 (d, 1H), 6.37 (dd, 1H), 7.22-7.38 (m, 15H), 7.86 (s, 1H), 8.11 (s, 1H).
13. Compound **5**, a mixture of two diastereomers : TLC(SiO_2, 9 : 1 ethyl acetate/methanol) R_f=0.80; IR 1210 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 80 MHz) δ 3.40-3.52 (m), 3.97-4.25 (m), 5.42-5.64 (m), 5.81-6.00 (m), 7.10-7.35 (m), 7.70-7.88 (m), 9.73 (brs).
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15. Compound **6** : TLC(SiO_2, 9 : 1 ethyl acetate/methanol) R_f=0.60; mp. 216-218℃ (Ref.[3], mp. 217-219℃); ^{1}H-NMR ($CDCl_3$, 80 MHz) δ 3.15 (d, 1H), 3.52 (d, 2H), 4.08-4.39 (m, 3H), 5.37 (d, 1H), 5.86 (d, 1H), 7.22-7.46 (m, 15H), 7.94 (d, 1H).
16. Compound **7** : mp. 209-211℃ (Ref.[2], mp. 208.5-215℃); $[\alpha]^{25}_D$ +126.5 (c 0.5, H_2O) (Ref.[2], +126); ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 3.90-4.04 (m, 2H), 4.05-4.15 (m, 1H), 4.23 (dd, 1H), 4.52 (dd, 1H), 5.97 (d, 1H), 6.29 (d, 1H), 7.96 (d, 1H).

Synthesis of 4-Carbethoxy-5-aryl-5,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-Dioxides

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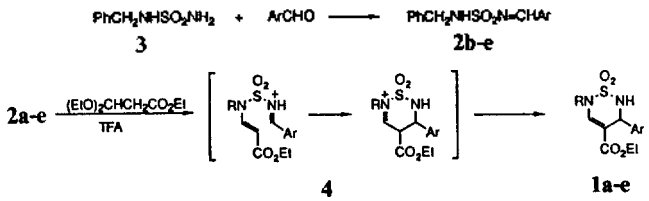
In recent years an increasing number of articles describing the synthesis, properties and biological activities of various heterocycles containing sulfamide unit have appeared,[1] and we have demonstrated that the intramolecular α-sulfamidoalkylation transformations of N-alkylsulfamides could provide those kinds of heterocycles, such as 5,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide derivatives.[2] Two general, acid-mediated procedures have been reported for the preparation of such 1,2,6-thiadiazine 1,1-dioxides.[3] The first entails the reaction of sulfamides with an equimolar amounts of 1,3-difunctionalized compounds and the second process entails the treatment of sulfamides with two equivalents of a carbonyl compound containing an acidic alpha hydrogen.

Table 1. Synthesis of N-Arylidenesulfamides **2** and 1,2,6-Thiadiazine 1,1-Dioxides **1**

Compound	mp. (℃)	yield (%)	Compound	mp (℃)	yield (%)
2a[2b]	105-106	65	**1a**	oil	42
2b	106-108	75	**1b**	122-124	50
2c	81-83	68	**1c**	oil	43
2d	118-120	81	**1d**	116-118	53
2e	130-133	73	**1e**	oil	40

We now wish to report on the use of the above α-sulfamidoalkylation process for the preparation of 4-carbethoxy-5-aryl-5,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxides **1** from N-arylidenesulfamides **2** and ethyl 3,3-diethoxypropionate in trifluoroacetic acid.



a R=H, Ar=phenyl. **b** R=benzyl, Ar=phenyl. **c** R=benzyl, Ar=1-naphthyl. **d** R=benzyl, Ar=4-methoxyphenyl. **e** R=benzyl, Ar=4-bromophenyl

N-Benzylidenesulfamide (**2a**) and N-benzylsulfamide (**3**) were prepared following the known procedures[2b,4,5] and the N-arylidene-N'-benzylsulfamides **2b-e** were prepared by condensing aromatic aldehydes with N-benzylsulfamide (**3**) in the presence of *p*-toluenesulfonic acid (see Table 1). Reaction of these N-arylidenesulfamides **2** with ethyl 3,3-diethoxypropionate in trifluoroacetic acid then afforded the 4-carbethoxy-5-aryl-5,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxides **1** (see Table 1) by undergoing intramolecular α-sulfamidoalkylation process through iminium ion **4**.

The typical procedure for the synthesis of **1** is as follows: A solution of **2d** (305 mg, 1 mmol) and ethyl 3,3-diethoxypropionate (190 mg, 1 mmol) in trifluoroacetic acid (10 m*l*) was stirred at rt for 48 hr and then concentrated in vacuo. Column chromatography (chloroform) of the residue afforded 220 mg (53% yield) of **1d**: IR (KBr) 3350, 1705, 1355, 1125 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.97 (t, 3H, J=7.0, $-CH_3$), 3.77 (s, 3H, $-OCH_3$), 3.92-3.97 (m, 2H, $-OCH_2-$), 4.63 (d, 1H, J=15.2 Hz, CH_2Ph), 4.68 (d, 1H, J=8.2 Hz, CHAr), 4.75 (d, 1H, J=15.2 Hz, CH_2Ph), 5.50 (d, 1H, J=8.2 Hz, NH), 6.83 (d, 2H, J=11.6 Hz), 7.20 (d, 2H, J=11.6 Hz), 7.35-7.45 (m, 5H), 7.38 (s, 1H, =CH-) ppm; ^{13}C-NMR ($CDCl_3$) δ 13.88, 52.37, 55.21, 59.14, 60.33, 108.00, 114.02, 128.34, 128.49, 128.92, 129.00, 129.48, 130.16, 134.85, 140.77, 159.58 ppm.

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