Table I. Thermal Decompositions of the Sulfoxides and (Phenylazo)diphenylmethane in the Presence of *cis*-β-Deuteriostyrene at 120 °C

radical source (concn, 10^4 M)	*cis*-styrene, 10^4 M	C_6D_6, mL	pyridine-d_5, mL	trans/cis ratio at ≅50% convn (convn, %; reactn time, min)
p-Tol-S(O)$CHPh_2$ (3.3)	4.3	0.40	0.01[a]	0.67 (58,[b] 30)
$CH_3S(O)CHPh_2$ (4.3)	4.3	0.40	0.01[a]	0.26 (55,[c] 30)
$CH_3S(O)CHPh_2$ (4.3)	4.3		0.40	0.44 (55,[c] 45)
$PhN{=}NCHPh_2$ (3.7)	4.3	0.40		0.00 (51,[c] 240)

[a] A small amount of pyridine was added to inhibit the ionic reaction.[1] [b] Calculated from the rate constant in ref 1. [c] Measured from NMR by using the area ratios of total phenyl protons vs. methyl or methine protons of the radical sources.

in its homopolymerization at 250 °C.[9] Reactions 1 and 2 are responsible for these isomerizations. It is clear that

$$\sim S(O_2)CH_2CH(Ph)\cdot \rightarrow \sim SO_2\cdot + {}^1/_2 cis\text{-styrene} + {}^1/_2 trans\text{-styrene} \quad (1)$$

$$\sim CH_2CH(Ph)CH_2CH(Ph)\cdot \rightarrow \sim CH_2CH(Ph)\cdot + {}^1/_2 cis\text{-styrene} + {}^1/_2 trans\text{-styrene} \quad (2)$$

the low bond dissociation energy of the carbon–sulfur bond makes reaction 1 rapid even at low temperature (50 °C). The isomerization observed in the present study can be explained similarly, namely, by addition–elimination reactions of sulfinyl radicals (eq 3 and 4[10]). Table I shows

$$CH_3S(O)\cdot + cis\text{-styrene} \rightarrow CH_3S(O)CH_2CH(Ph)\cdot \text{ (or } CH_3SOCH_2CH(Ph)\cdot) \quad (3)$$

$$CH_3S(O)CH_2CH(Ph)\cdot \text{ (or } CH_3SOCH_2CH(Ph)\cdot) \rightarrow CH_3SO\cdot + {}^1/_2 cis\text{-styrene} + {}^1/_2 trans\text{-styrene} \quad (4)$$

the molar ratio of *trans*- to *cis*-styrene at nearly 50% conversion. From the table it can be seen that BTSO in benzene-d_6 and BMSO in pyridine-d_5 also isomerize *cis*-styrene considerably.

Other isomerization mechanisms without involving sulfinyl radicals may be excluded from the results in Table I. (Phenylazo)diphenylmethane was used to check that isomerization was not induced by benzhydryl radical, which is another radical formed in decompositions of the sulfoxides. Table I shows that thermal decomposition of (phenylazo)diphenylmethane in the presence of *cis*-styrene in benzene-d_6 at 120 °C, half-life period of which is about 240 min from NMR, gave no *trans*-styrene after the half-life period. In this reaction polystyrene was formed and styrene concentration gradually decreased.

Boothe, Greene, Shevlin, Willcott, Inners, and Cornelis[7] have found that the β-phenylsulfinyl *sec*-butyl radical eliminates the phenylsulfinyl radical and the elimination is so rapid that the formations of 2-butenes are stereoselective when diastereomeric precursors are used. Our conclusion that sulfinyl radicals may add styrene but that its reverse reaction is much faster is in accord with their findings and it can explain an inertness of sulfinyl radicals toward olefinic compounds described before.

Experimental Section

General Remarks. NMR spectra were obtained by using a JEOL JNM-PS-100 (100 MHz) spectrometer.

Materials. *cis*-β-Deuteriostyrene (KOR ISOTOPES) was uses without further purification. The content of *cis*-styrene was over 99% from NMR analysis. Benzhydryl *p*-tolyl sulfoxide (BTSO) and benzhydryl methyl sulfoxide (BMSO) were prepared by the method described in the previous paper.[1] (Phenylazo)diphenylmethane was prepared by the method of Cohen and Wang[11] and checked for purity by NMR analysis of the methine proton (δ 6.14 in benzene-d_6, singlet).

Thermal Decompositions of BTSO, BMSO, and (Phenylazo)diphenylmethane in the Presence of *cis*-β-Deuteriostyrene. Degassed and sealed NMR tubes containing radical precursor (BTSO, BMSO, or (phenylazo)diphenylmethane) and *cis*-styrene in benzene-d_6 (see Table I) were immersed in a water bath regulated at 120 °C, and NMR measurements were taken at room temperature after the tubes were cooled to stop the reaction at regular time intervals. The main products in BTSO or BMSO decompositions are the coupling products, namely, the corresponding thiosulfonates ($RSS(O_2)R$) and tetraphenylethane, like the case without styrene in the previous paper,[1] and for (phenylazo)diphenylmethane, polystyrene and tetraphenylethane were identified from the NMR spectrum of the reaction mixture.

As shown in Table I a small amount of pyridine-d_5 was added in the decompositions of BTSO (or BMSO) in benzene-d_6, since the absence of pyridine gave products such as benzhydryl *p*-tolyl sulfone, bis(diphenylmethyl) ether, *p*-tolyl disulfide, and benzhydryl *p*-tolyl sulfide other than the coupling products (the thiosulfonate and tetraphenylethane), which may be formed by ionic reactions.[1]

Registry No. p-Tol-S(O)$CHPh_2$, 5427-07-6; $CH_3S(O)CHPh_2$, 2863-45-8; $PhN{=}NCHPh_2$, 61765-91-1; *cis*-β-deuteriostyrene, 21370-59-2.

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[9] Chang, K. M.; Yamaguchi, T.; Iino, M.; Matsuda, M., unpublished results.

[10] $^1/_2$ in eq 4 is rigorously uncorrect due to secondary isotope effects and the difference of stability in *cis*- and *trans*-styrene, but these effects are estimated to be very small.

[11] Cohen, S. G.; Wang, C. H. *J. Am. Chem. Soc.* **1955**, *77*, 3628.

Photoinitiation of the $S_{RN}1$ Reaction by Excitation of Charge-Transfer Complexes

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Received January 27, 1983

Extensive studies during the last decade of $S_{RN}1$ aromatic substitutions have demonstrated the importance of this reaction class, both from a mechanistic and synthetic viewpoint.[1,2] Substitutions proceeding by this mechanism can be effected under mild conditions and without the use of highly activating substituents. Because of the myriad of synthetically useful transformations brought about in this fashion, definitive work is now available which characterizes both the propagation[3] cycle, summarized in Scheme I and the termination[4] steps of this reaction.

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[2] Saveant, J. M. *Acc. Chem. Res.* **1980**, *13*, 323.

[3] Kim, J. K.; Bunnett, J. F. *J. Am. Chem. Soc.* **1970**, *92*, 7463, 7464.

[4] Amatore, C.; Pinson, J.; Saveant, J. M.; Thiebault, A. *J. Am. Chem. Soc.* **1981**, *103*, 6930.

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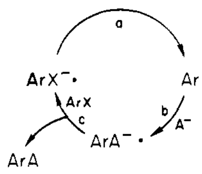
Scheme I



ArX = aryl halide
A⁻ = anion

A complete mechanistic description of this reaction thus requires characterization of the initiation step. Several modes of initiation are known: injection of solvated electrons into the reaction medium by addition of dissolving metals, electroreduction of the aryl halide, or photoexcitation of the reaction melange. The first two modes are quite similar and have been described by Saveant and co-workers.[5] The exact nature of the last mode, photostimulation, remains ambiguous, however.

Hoz and Bunnett attempted to characterize the mechanistic details of photoinitiation in the reaction of iodobenzene with diethyl phosphite ion.[6] From quantum yield measurements, they could establish that photolysis was accomplished in one of three ways: (a) homolytic cleavage of the aryl–iodine bond, eq 1, producing an aryl radical that

$$\text{Ar–I} \xrightarrow{h\nu} \text{Ar}\cdot + \text{I}\cdot \qquad (1)$$

enters the propagation cycle at step b, (b) electron transfer from the anion to the excited iodobenzene, eq 2, generating

$$\text{Ar–I} \xrightarrow{h\nu} \text{ArI}^* \xrightarrow{\text{A}^-} \text{ArI}^{-}\cdot + \text{A}\cdot \qquad (2)$$

a radical anion that allows entry at step a, or (c) electron exchange within an excited charge-transfer complex, eq 3, leading to a species that enters the propagation cycle

$$[\text{ArI}\cdots\text{A}^-] \xrightarrow{h\nu} [\text{ArI}^{-}\cdot\cdots\text{A}\cdot] \rightarrow \text{ArI}^{-}\cdot + \text{A}\cdot \qquad (3)$$

at a, b, or c.

We describe in this paper wavelength-dependent quantum yield measurements which identify electron transfer within an excited charge-transfer complex as a sufficient photoinitiation mode for two photostimulated $S_{RN}1$ reactions but insufficient for a third. We chose for our studies three previously studied photostimulated reactions that proceed in high chemical yield, the reactions of acetone enolate (1) with iodobenzene (2)[7] or with bromobenzene (3)[8] to give phenylacetone (88% and 94%, respectively) and of potassium diethyl phosphite (4) with iodobenzene to produce diethyl phenylphosphonate (68%).[7]

Results and Discussion

Evidence for complexation is apparent upon bringing the required reagents into contact. For example, if a yellow solution of anion 4 is mixed with a colorless solution of 2, an intense purple color develops. The ultraviolet (UV) absorption spectra of the individual components and the mixture of 2 and 4 are shown in Figure 1. The enhanced absorptions, red-shifted into the visible- and long-wavelength UV spectral regions, observed upon mixing the reagents has been ascribed to the formation of a ground-state charge-transfer complex because the individual components of the reaction mixture can be recovered unchanged if the purple solution is shielded from light and quenched by addition of dilute acid. Analogous spectral changes are observed also in the other mixtures. Since the individual components are optically transparent at wavelengths greater than 400 nm,[9] selective excitation of the charge-transfer bands is possible in this region.

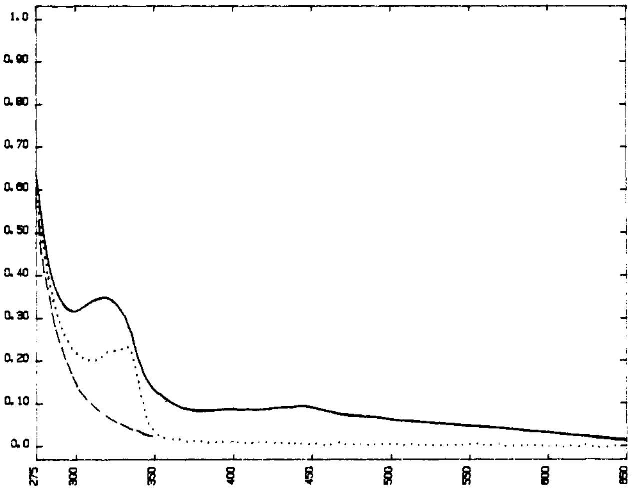


Figure 1. Absorption spectra: ..., iodobenzene (8×10^{-4} M); - - -, potassium diethyl phosphite (8×10^{-4} M); —, complex formed upon mixing iodobenzene (8×10^{-4} M) and potassium diethyl phosphite (8×10^{-4} M).

Table I. Relative Quantum Yields for Photostimulated $S_{RN}1$ Reactions

anion	concn, mol/L	ArX	concn, mol/L	Φ/Φ_{ctc}
1	0.33	2	0.08	1.0 ± 0.1
1	0.33	3	0.08	1.1 ± 0.1
4	0.25	2	0.11	3.4 ± 0.4

If the quantum yields for photoreaction with wavelengths greater than 400 nm (Φ_{ctc}) are compared with those found at wavelengths greater than 200 nm (ϕ, where extensive excitation of the aryl halide, the solvent, or the uncomplexed anion would also occur), the relative importance of charge-transfer-complex-absorbed photons in the photoinitiation can be determined. Since the photoreaction stimulates a radical chain process which is sensitive to impurity termination, best reproducibility was obtained by expressing the results of matched pairs of solutions as ratios of quantum yields for charge-transfer and nonselective irradiation. The ratios so obtained are shown in Table I.

That the reaction can be initiated with complex-absorbed photons implies that some route exists from the excited complex to the propagation cycle. Previous studies have shown that photoexcitation of charge-transfer complexes, species which are usually only slightly more stable than the free components, gives rise to a nonrelaxed state to which several fates are possible.[10] This state can relax to equilibrium through a reorientation of the components and solvent molecules, decay radiationlessly to the ground state, give rise to local triplet formation,[10-12] or dissociate to solvent-separated radical ions through the radical ion pair.[13-17] The first two fates would be energetically dis-

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(5) Amatore, C.; Chaussard, J.; Pinson, J.; Saveant, J. M.; Thiebault, A. *J. Am. Chem. Soc.* **1979**, *101*, 6012.

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(9) With wavelengths only longer than 400 nm, Me_2SO solutions of both iodobenzene and bromobenzene can be recovered unchanged even after prolonged irradiation.

(10) Wong, P. C.; Arnold, D. R. *Can. J. Chem.* **1980**, *58*, 918.

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sipative and hence useless for photoinitiation.[18] If the third route is taken, homolytic fission of the carbon–halogen bond might be anticipated,[19] and initiation via the phenyl radical might be achieved. Electron transfer through the last route initiates the sequence described in eq 3. Although both the third and fourth routes may ultimately produce a phenyl radical, it is extremely unlikely that the efficiency of excited triplet-state production attained by back electron transfer within an excited charge-transfer complex would be identical with that obtained by direct irradiation.

That identical quantum efficiencies are observed upon excitation of the charge-transfer bands in the **1**–**2** and **1**–**3** systems as with nonselective broad-band irradiation is consistent with electron transfer within an anion–aryl halide complex in the primary photoinitiation step. That diminished importance of charge-transfer excitation is observed with **2**–**4** implies that some other mechanism, possibly that described in eq 1, must compete with photoinduced electron transfer as the primary photoprocess, unless the electron transfer within the excited charge-transfer complex is wavelength dependent. While wavelength dependence has been reported for some olefin charge-transfer complexes,[17,20] wavelength-dependent phenomena emanating from a single excited state remain rare in organic photochemistry.[21]

The facility of electron transfer within the complex should depend on the energy difference between the reduction potential of the aryl halide and the oxidation potential of the anionic donor. Using literature values for the reduction potentials and estimating anion oxidation potentials by extrapolation from pK_a measurements,[22] we estimate that electron transfer from **1** to **2** (+0.7 V) and from **1** to **3** (+1.0 V) are less endothermic than the energy available from photon absorption at the 0,0 band of the charge-transfer complex ($\lambda \approx 700$ nm, 1.75 V). The electron transfer within the **2**–**4** excited complex (+1.4 V), however, is less favorable and may in fact be endothermic if as little as 7 kcal/mol thermal activation is required for reorientation within the complex. Electron transfer within this charge-transfer complex would then be less important than alternate pathways available through direct irradiation, e.g., aryl halide homolysis.

It is reasonable to suggest therefore that the relative efficiencies for electron-transfer initiation within charge-transfer complexes might be predicted from the redox potentials of the component partners together with absorption band positions of the charge-transfer complexes. In fact, with systems in which such electron transfer is predicted to be exothermic without excitation, e.g., **1** with 9-bromoanthracene, we find that photostimulation is unnecessary, the required electron transfer apparently being initiated by vibrational distortions within the charge-transfer complex. It is possible therefore that these studies will provide valuable clues to the nature of the heretofore puzzling thermal activation of some $S_{RN}1$ reactions.[23]

While we are at present gathering information to distinguish less ambiguously local excited-state production from electron exchange within the excited charge-transfer complex, our results do show clearly that charge-transfer-complex excitation represents a significant fraction of $S_{RN}1$ photostimulation. Further consequences of this finding are being sought.

Experimental Section

Instrumentation and Materials. Ultraviolet and visible absorption spectra were obtained on a Hewlett-Packard 8450A spectrophotometer. Nuclear magnetic resonance (NMR) spectra were obtained on a Varian EM-390 spectrometer. Gas–liquid chromatography (GLC) was conducted on an Antek 400 flame-ionization instrument equipped with 5 ft × $^{1}/_{8}$ in. columns. Peak intensities were monitored with a Hewlett-Packard 3390A digital integrator. The irradiation source was a 1000-W high-pressure mercury–xenon lamp or a 250-W high-pressure mercury lamp (Applied Photophysics) mounted on a optical train, with or without a Corning 3-73 sharp cutoff filter ($\lambda \approx 400$ nm).

Diethyl phosphite and dimethyl sulfoxide (Me_2SO) were stirred over CaH_2 and distilled under vacuum. Potassium *tert*-butoxide was freshly sublimed. Iodobenzene was dried over CaH_2, distilled, and stored protected from light. Analytical-grade bromobenzene and spectral-grade acetone were used without further purification.

Reaction of Acetone Enolate (1) and Iodobenzene (2). The procedure followed was similar to that described by Bunnett, Scamehorn, and Traber.[7] The deep-brown solution obtained by mixing acetone enolate (10 mmol) with iodobenzene (2.4 mmol) was irradiated for 1 h (3.8 h when filtered) with a focused high-pressure mercury lamp. The reaction was quenched with 60 mL of water and extracted three times with ether. The organic layer was analyzed by GLC (5% SE-30 on Chromosorb P, 130–230 °C at 4°/min, biphenyl internal standard). The major product isolated was phenylacetone (88%), although a number of unidentified minor products could be detected in trace quantity.

Reaction of Acetone Enolate (1) and Bromobenzene (2). In a procedure similar to that described above, the enolate derived from 0.73 mL (10.0 mmol) of acetone was allowed to react with 0.25 mL (2.4 mmol) of bromobenzene. After irradiation of the bright yellow charge-transfer complex with a high-pressure mercury lamp for 1.25 h (6 h filtered), the solution became orange. After workup as described above, phenylacetone was obtained in 94% yield.

Reaction of Potassium Diethyl Phosphite (4) and Iodobenzene (2). The method of Hoz and Bunnett[6] was employed. The initially yellow solution of potassium diethyl phosphite (7.5 mmol) turned a deep purple upon addition of iodobenzene (3.25 mmol). The solution was irradiated for 5 h (13 h filtered) with a mercury–xenon lamp. After the solution was quenched with 60 mL of water, the aqueous layer was extracted three times with ether. The organic layer was concentrated and analyzed by GLC (5% SE-30 on Chromosorb P, 130–200 °C at 4°/min, dodecane internal standard). Diethyl phenylphosphonate was obtained in 68% yield.

Determination of Quantum Yields. Quantum yields were obtained on a light-shielded optical bench by using the filtered and unfiltered emission of a high-pressure mercury lamp. The focused light beam was split, with the sample and an actinometer cell being simultaneously irradiated for a measured period. A backup actinometer cell was placed in the optical path behind the sample cell to correct for partial absorption of incident photons. Photon flux was measured with a 0.15 M solution of potassium ferrioxalate according to the method of Hatchard and Parker,[24] and disappearance of aryl halide and appearance of products were followed quantitatively by GLC (see above). The results obtained, expressed as the ratio of quantum yields for the unfiltered and filtered light source, are listed in Table I.

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(18) Absolute values of the quantum efficiencies of these reactions cannot rule out energy-dissipative back electron transfer, since even if the quantum yield for initiation is itself low, the occurrence of a chain process will amplify the importance of the effective photoinitiation.

(19) For reviews of ArX photochemical cleavages, see: Fox, M. A. In "Aromatic Photosubsitutions"; Parkanyi, C., Ed.; Plenum Press: New York, in press. Kharasch, N.; Sharma, R. K. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 36.

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Acknowledgment. Support of this work by the National Science Foundation and by the Robert A. Welch Foundation is gratefully acknowledged. M.A.F. is grateful for support as an Alfred P. Sloan Research Fellow and as a Camille and Henry Dreyfus Teacher–Scholar.

Registry No. **1**, 71695-00-6; **2**, 591-50-4; **3**, 108-86-1; **4**, 54058-00-3.

Synthesis of 2′-*O*-(1,3-Benzodithiol-2-yl)uridine and Related Compounds as Key Intermediates in Oligoribonucleotide Synthesis

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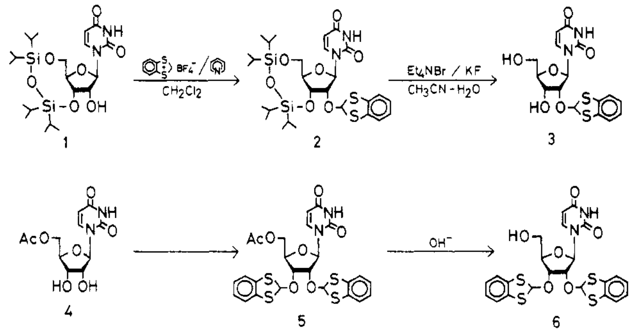
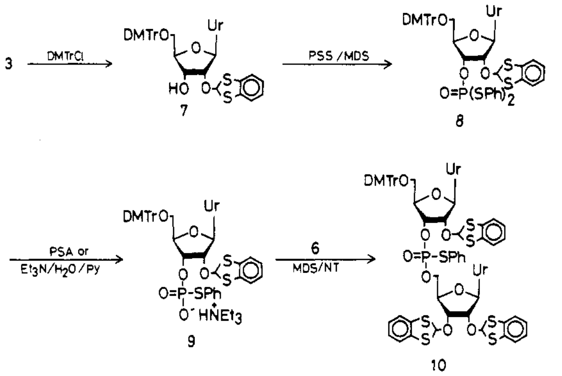
Received November 2, 1982

In a previous paper,[1] we reported a new protecting group, 1,3-benzodithiol-2-yl (BDT), designed for nucleoside hydroxyl functions. The BDT group has proved to be readily introduced into primary and secondary hydroxyl groups and removed under mildly acidic conditions. This paper describes the utility of the BDT group as a 2′-hydroxyl protecting group.[2-5] When a cyclic silylated uridine derivative (**1**)[6] was allowed to react with 1.5 equiv of 1,3-benzodithiolium tetrafluoroborate (BDTF), the 2′-*O*-(1,3-benzodithiol-2-yl)uridine derivative **2** was obtained in 80% yield. In this reaction, the N^3-alkylation occurred competitively with the 2′-O-alkylation. However, the dialkylated product was unstable during chromatography and was decomposed to **2**. In a similar manner, 5′-*O*-acetyluridine (**4**) reacted with BDTF to give the 2′-O-alkylated product **5** in 77% yield. In this case, an unstable N^3-alkylated product was also detected.[7]



Next, we prepared two key intermediates **3** and **6** for the synthesis of oligoribonucleotides from **2** and **5**, respectively. Fluoride ion mediated deprotection[8] of **2** gave **3** in 94% yield. On the other hand, alkaline hydrolysis of **5** afforded **6** in 88% yield. Compound **6** was also obtained in good yield from **4** without purification of **5**.

Next, the synthesis of uridylyl (3′→5′)uridine was examined by using **3** and **6** in order to ascertain their usefulness. The compound **8** was synthesized in high yield by the usual dimethoxytritylation followed by phosphorylation with cyclohexylammonium *S*,*S*-diphenyl phosphorodithioate (PSS)[9] in the presence of mesitylene-1,3-disulfonyl chloride (MDS).[10] Selective removal of one phenylthio group was performed in two ways. The first of these was use of phosphinic acid (PSA)–triethylamine–pyridine[1,7,9] as previously described by us. The other involves basic conditions, i.e., triethylamine–water–pyridine.[1] Although the latter method was simple and gave a mixt. of diester **9** and thiophenol upon evaporation, the reaction required 5 h. In contrast with this result, a phenylthio group was removed from **8** within 15 min when a 3.3 M solution of PSA buffered with triethylamine in pyridine was employed. We previously reported that thiophenol, a byproduct of the extractive workup, did not affect the condensation of a diester with a hydroxyl component.[1,11] Therefore, the mixture of the triethylammonium salt of **9** and thiophenol was allowed to react with **6** in the presence of MDS and 3-nitro-1,2,4-triazole (NT). This coupling proceeded smoothly and gave dimer **10** in 76% yield. The dimer **10** was successfully converted to UpU by treatment with 0.2 M NaOH–dioxane or a silver ion catalyzed dephenylthiolation,[9] followed by treatment with 0.01 M HCl (pH 2.0)[12] The unprotected dimer was isolated in more than 91% yields by paper chromatography and analyzed by snake venom and spleen phosphodiesterases, whereupon the correct ratios of the degradation product were obtained.



These results suggest that the BDT group can be used as a useful protecting group of the 2′-hydroxyl and 2′,3′-cis-diol functions.

Since the BDT group has a stability similar[1] to that of the 4-methoxytetrahydropyran-4-yl group[4,7] under acidic conditions, chain elongation of oligoribonucleotides will be realized by employing the levulinyl[13] and fluoren-9-ylmethoxycarbonyl[14] groups, recently reported by van

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(7) It is interesting that compound **5**, protected with the two BDT groups, could be obtained since we have failed to obtain 5′-*O*-acetyl-2′,3′-di-*O*-(4-methoxytetrahydropyran-4-yl)uridine by the pyranylation of **4** under usual conditions (Reese, C. B.; Saffhill, R.; Sulston, J. E. *J. Am. Chem. Soc.* **1967**, *89*, 3366, and see also ref 4). The successful introduction of the BDT groups into the cis diol of **4** may be attributed to the avoidance of 2′,3′-cyclic acetal formation by employing almost neutral rather than acidic conditions in the case of the pyranylation.

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