olefin adducts when crotonaldehyde is employed. Ketones undergo efficient photocycloaddition in a nonstereoselective manner, but with enhanced chemoselectivity (7:1) favoring addition to the less substituted olefin of 2-methylfuran. In a single example, we have observed that thiophene undergoes photocycloaddition with benzaldehyde to afford a single exo photoadduct.[11]

Functionalization of the photoaldols can be carried out in a variety of manners as depicted in Schemes I and II. Hydrolysis (1:4 0.01 N HCl-THF, room temperature, 0.5 h) of **1a** and **1b** afforded the site-specific threo-aldolized 1,4-dicarbonyl compounds **2a** and **2b**, respectively, in 88-92% yield.[8,11] Methanolysis (CSA, MeOH, room temperature, 0.5 h) of **1a** and **1b** provided the rearranged tetrahydrofurans **3a** and **3b**, respectively, each as a single stereoisomer, in 94% yield.[8,11] Hydrogenation (1 atm of H_2, 5% Rh/Al_2O_3, Et_2O, 6 h) from the convex face of **1a** proceeded smoothly to afford a labile ketal oxetane (not isolated) which was hydrolyzed to the diol **4a** (R^1 = H) after filtration through wet Celite. The diol **4a** existed in equilibrium with its corresponding hemiketols and was most easily characterized as the bis-acetate (R^1 = Ac) after acetylation (Ac_2O, Et_3N, DMAP, CH_2Cl_2, O °C) in overall 78% yield from **1a**.[8,11]

To demonstrate the feasibility of forming carbon-carbon bonds to the β-carbon of the enol ether, inverse demand heterodiene Diels-Alder reaction was carried out with **5a** and Tietze's reagent ($HC(CHO)_3$).[12] Cycloaddition ($CHCl_3$, 67 °C, 4 h) occurred to produce two inseparable adducts, **6** and **7**,[8,11] with 7:1 stereoselectivity in 45% yield.[13] The corresponding acetates were readily separated and characterized individually.

Several oxidative functionalization procedures wre investigated. For example, epoxidation (MCPBA, $NaHCO_3$, CH_2Cl_2, room temperature, 2 min)[14] of **5a** and **5b** afforded the corresponding β-hydroxytetrahydrofurans **8a** and **8b**, respectively, in 85-88% yield.[8,11] Acetylation of **8a** and **8b** was carried out to further characterize and demonstrate the stability of these substances. Similar oxidation of **9a** and **9b** afforded **10a** and **10b**, respectively, in 80-84% yield.[11] All five chiral centers present in **10** are suitably disposed for application to the synthesis of asteltoxin,[15] a project under investigation in our laboratories.

Hydroboration-oxidation (BH_3·THF (inverse addition), $H_2O_2/NaOH$) of the photoaldol **11** resulted in the anti-Markovnikov hydration of the enol ether[16] and hydrogenolysis of the acetal[17] to afford the 1,3-diol **12** in 40% yield. Subjection of **13** to similar conditions afforded the 1,3-diol **14** in 82% yield, *resulting in total stereocontrol over five contiguous chiral centers in a two-step procedure*. The stereochemistry of **14** (and the corresponding bis-acetate) was apparent from the 500-MHz ^1H NMR spectrum and was verified by single-crystal X-ray diffractometry[18] on the corresponding bis(*p*-bromobenzoate) derivative. Structure determination by this method establishes in an unambiguous manner the threo outcome[9] of the photocycloaddition reaction, syn-convex addition of the boron reagent, and hydrogenolysis with retention of configuration. The stereochemistry of the hydrogenolysis can be explained by the mechanism in Scheme II. Boron-mediated oxetane ring opening followed by internal delivery of hydride results in the replacement of the carbon-oxygen bond with a carbon-hydrogen bond with retention of configuration.

In summary, the methodology described represents a stereocontrolled route to highly functionalized systems that should find application in synthesis. In addition, the intramolecular furan-carbonyl photocycloaddition will be reported shortly and should enhance the overall utility of this methodology.

Acknowledgment. We gratefully acknowledge financial support from the Camille and Henry Dreyfus Foundation and the Chicago Community Trust/Searle Scholars Program. NMR spectra were obtained through the auspices of the Northeast Regional NSF/NMR Facility at Yale University, which was supported by the NSF Chemistry Division Grant CHE 7916210. Experimental assistance from Kunio Satake is greatly appreciated.

Supplementary Material Available: Table I containing results for 23 furans and carbonyl compounds (2 pages). Ordering information is given on any current masthead page.

(11) All compounds reported gave ^{13}C NMR (22.6 MHz), ^1H NMR (500, 270, or 90 MHz), IR, and mass spectra (low resolution) in accord with the structure given. Exact mass calculations (CI) were performed on all functionalized photoaldol products.

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(13) The acidic Tietze reagent catalyzes a retro[2 + 2] pathway to afford furan and the aldehyde in 40% yield. In the other functionalization procedures, the retro[2 + 2] reaction occurs to an extent of 0-25%.

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(18) We gratefully acknowledge Professor J. M. McBride and Bruce Weber for carrying out the X-ray structure determination. Full details of the crystal data will be published separately.

Hindered Dialkylamino Nucleoside Phosphite Reagents in the Synthesis of Two DNA 51-Mers†

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Received November 1, 1982

Recent dramatic developments in recombinant DNA technology have been accompanied by equally impressive advances in the rapid chemical synthesis of DNA. In addition to utilizing the classical phosphate triester approach,[1-4] significant improvements have been realized by the application of phosphite triester chemistry[5-9] and, more recently, by the development of nucleoside phosphoramidite reagents **2**.[10] Additionally, the implementation of solid supports[7,8,11-14,20] has greatly simplified DNA synthesis by eliminating intermediate purification steps.

In this communication, we report the application of significantly improved nucleoside phosphoramidite reagents to DNA synthesis on a superior solid support.

Our experience with dimethyl phosphoramidites **2** dictated a need for improved solution stability. Consequently, a series of

† Presented at the 183rd Meeting of the American Chemical Society, Las Vegas, NV, March 1982.

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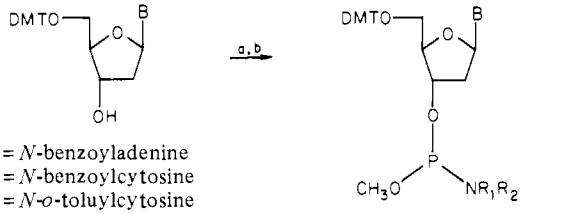
Scheme I



1a, B = *N*-benzoyladenine
b, B = *N*-benzoylcytosine
c, B = *N*-*o*-toluylcytosine
d, B = *N*-isobutyrylguanine
e, B = thymine

2, $R_1 = R_2$ = methyl
3, $R_1 = R_2$ = ethyl
4, R_1 = methyl; R_2 = isopropyl
5, $R_1 = R_2$ = isopropyl

[a] $ClP(OCH_3)NR_1R_2$ (2 equiv), diisopropylethylamine (4 equiv), THF, room temperature. [b] 10% sodium carbonate workup, precipitate in −70 °C hexane.

Table I. Stabilities of Nucleoside Phosphites 2-5 ($t_{1/2}$, h)[a]

	2 (Me_2)[b]	3 (Et_2)	4 (Me, *i*-Pr)	5 (*i*-Pr_2)
DMT-dA^{bz}		45		>96[d]
DMT-dC^{bz}	12	30		>96[d]
DMT-dC^{tol}		~120[c]		
DMT-dG^{ib}		48		>96[d]
DMT-dT		144	~144[c]	>96[d]

[a] Stability determined by disappearance of phosphite peaks in the ^{31}P NMR spectrum; ~0.1 M solutions in acetonitrile. The values obtained vary somewhat between preparations and should be used for comparison. [b] Values in this series vary, but all are less stable than their ethyl counterparts by a factor of 2–4. [c] A small amount of precipitate formed. [d] Virtually no decomposition after 4 days.

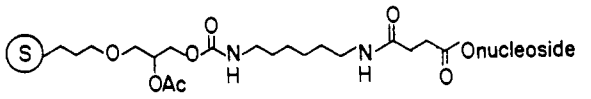
Table II. Reactivities of Phosphites on Silica Support

reagent	amount[a]	dinucleotide yield, %
2e (Me_2)	15	80–90
	30	95
3e (Et_2)	15	92–97
	30	97
5b (*i*-Pr)	15	73

[a] 50-mg support (4 μmol of nucleoside) + 15–30 equiv of phosphite (0.25 mL of dry CH_3CN) + 60–120 equiv of tetrazole (0.5–0.7 mL of dry CH_3CN), 15 min.

compounds, **3–5**, were prepared[10,15] (Scheme I), which exhibit increased steric encumberance about the labile P–N bond. As is apparent from Table I, this steric hinderance leads directly to increased reagent stability in solution. Additionally, phosphite instability in the deoxycytidine series, the least stable of the four nucleoside reagents, can be tied in part to the nature of the amide protecting group—the diethyl derivative **3c** protected just as the more stable *o*-toluamide[16] is more stable than **3b**.

The usefulness in DNA synthesis of these hindered reagents required that the high reactivity characteristic of their chloro and dimethylamino counterparts not be unduly compromised. For a test of their reactivity with nucleosides on solid supports, silica functionalized with thymidine was prepared[7] and detritylated ($ZnBr_2$, 5% methanol/nitromethane), and 50-mg portions were submitted to varying condensation conditions (Table II). Following oxidation[5] and removal of the phosphate protection group,[9] the trityl-protected dinucleotide and mononucleoside were removed from the support and assayed by HPLC.[17,18] Interestingly, even large excesses of reagent failed to completely consume the supported nucleoside. Operating on the hypothesis that this was a support-induced steric effect, a new nucleoside support, **6**, was



6

prepared,[19] which gave outstanding results—the condensation reaction was essentially quantitative with an 8–10-fold excess of phosphoramidite, and the reaction appeared to be faster.

Actual DNA synthesis is achieved by the synthetic cycle outlined in Table III. A small amount of support (40 mg, ~1–2 μmol) functionalized with the nucleoside corresponding to the 3′ end of a desired sequence is placed in a reaction vessel[13] and treated with acid. Traditionally, strong protic acids such as benzenesulfonic acid and trichloroacetic acid (pK_a = 0.7) have been utilized, which very rapidly remove the trityl group; however, their use is complicated by the depurination of adenosine and, to a lesser extent, guanosine residues. As an alternative, zinc bromide[7,21,22] has been used, which does not cause significant depurination; however, the rate of trityl removal decreases rapidly as the DNA chain becomes longer,[23] effectively limiting the sequence length. An an altenative, we have implemented the use of dichloroacetic acid (pK_a = 1.5), which still removes the trityl group very rapidly[24] and causes only a minimum of depurination. After detritylation, the support is washed,[25] and phosphoramidite, preferably **5** (15 equiv, 0.25 mL of dry acetonitrile) is added under dry nitrogen by syringe and is then activated by tetrazole (40 equiv, 0.25 mL of dry acetonitrile). After oxidation and capping of any unreacted

Table III. Synthetic Cycle

reagent	vol, mL	time, min
1. 0.2 M DCA/CH_2Cl_2	2	2
2. CH_2Cl_2, CH_3CN wash	5	
3. CH_3CN/N_2 wash	2	
4. phosphite (15 equiv)/CH_3CH/N_2 +	0.25	
tetrazole (~40 equiv)/CH_3CN	0.25	2
5. CH_3CN wash		
6. 0.1 M I_2 in 1:2:2 2,6-lutidine/ THF/H_2O	1	1
7. CH_3CN, THF wash	5	
8. 0.1 M DMAP/THF + 1:2	1	2
AC_2O/2,6-lutidine	0.5	
9. CH_3OH, CH_2Cl_2 wash	5	

(15) Reagent purity depends on the absolute exclusion of acidic impurities achieved by filtering all solvents through basic alumina immediately prior to use. Reagents were >95% pure by ^{31}P NMR (δ, CH_2Cl_2 (external H_3PO_4)). **3a**: 148.8, 148.6. **3b**: 149.4, 149.1. **3c** (CH_3CN): 148.5, 149.1. **3d**: 148.0, 148.2. **3e**: 148.7, 148.1. **4e**: 147.1, 146.7. **5a**: 148.2, 148.0. **5b**: 148.3, 148.0. **5d**: 148.4, 148.2. **5e**: 148.1, 147.9. $ClP(OCH_3)N(CH_2CH_3)_2$: bp 87–89 °C (18 mmHg); δ (neat) 179.3. $ClP(OCH_3)N[CH(CH_3)_2]_2$: bp 83–86 °C (12 mmHg); δ (neat) 180.8. $ClP(OCH_3)N(CH(CH_3)_2)(CH_3)$: bp 62–64 °C (12 mmHg); δ (neat) 176.8.

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(17) Crude product mixtures were chromatographed as follows: Waters 10 μm C_{18} radial compression column, 30% acetonitrile, 70% 0.1 M triethylammonium acetate, pH 6.8, 2.2 mL/min flow rate. Retention times: dT = 1.0 min; DMT dinucleotide = 2.2 min; DMT-dT = 6.5 min. A trace of DMT-dT was the only significant contaminant (~1–4%). We thank Dr. Gary Mappes for this work.

(18) The attenuation of **5b** appears to be a support-induced steric effect rather than decreased intrinsic reactivity: Adams, S. P.; Galluppi, G. R., results to be published.

(19) The 3′-succinyl ester of **1e**[20] was condensed with "long chain alkyl amine" controlled pore glass (Pierce Chemical Co., Rockford, IL) by using 1-ethyl-3-(3-(dimethylamino)propyl)carbodiimide and (dimethylamino)-pyridine in DMF followed by capping with acetic anhydride/DMAP/DMF. Recently, this support has been utilized independently with phosphotriester chemistry: Gough, G. R.; Brunden, M. J.; Gilham, P. T. *Tetrahedron Lett.* **1981**, *22*, 4177–4180.

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(23) This effect has also been observed on a polystyrene support.[13]

(24) In all cases, detritylation of cytidine residues is slowest. This has been alleviated by the use of the trimethoxy trityl-protecting group.

(25) All washings are most easily performed by using plastic squeeze bottles.

nucleoside left on the support, another round of synthesis begins.[26]

The DNA is deprotected by using thiophenoxide[9] (1:2:2 thiophenol/triethylamine/THF, room temperature, 1 h), cleaved from the support (NH_4OH, room temperature, 1 h) and further deprotected by heating the supernatant at 50 °C overnight. Following evaporation of the supernatant, purification is accomplished by Sephadex G-50 chromatography followed by polyacrylamide gel electrophoresis.

The effectiveness of these developments in DNA synthesis is demonstrated by the synthesis of two complementary DNA 51-mers (A and B). Sequence A was synthesized in 10.5 h while

A GATCCTTCCCAGCCATGTCCTTGTCC-

B GAAGGGTCGGTACAGGAACAGG-

A GGCCTGTTTGCCAACGCTGTGCTCG

B CCGGACAAACGGTTGCGACACGAGCCTAG

strand B was prepared concurrently with four shorter sequences. Purified strands A and B were annealed and cloned in bacteriophage M13, and their sequences were verified by the Sanger dideoxy sequencing technique.[28]

In summary, we have extended the capabilities of DNA synthesis on solid supports by implementing hindered nucleoside phosphoramidites of significantly improved stability that react very rapidly on a new solid support that exhibits superior chemical and physical properties. These refinements have allowed the synthesis of two 51-mers, the longest DNA fragments synthesized chemically to date.

Supplementary Material Available: Analytical polyacrylamide gel data and M13 sequence information for A and B (2 pages). Ordering information is given on any current masthead page.

(26) The cycle requires only 8–10 min, and four to six reaction vessels can easily be manipulated simultaneously with a 20-min cycle time.

(27) Determined by a sensitive radiolabel assay of material purified by polyacrylamide gel electrophoresis. Crude yields as determined by trityl release in the final deprotection were ~10%.

(28) Sanger, F.; Nicklen, S.; Coulson, A. R. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 5463–5467.

Formation of an Ozonide by Electron-Transfer Photooxygenation of Tetraphenyloxirane. Cosensitization by 9,10-Dicyanoanthracene and Biphenyl[1]

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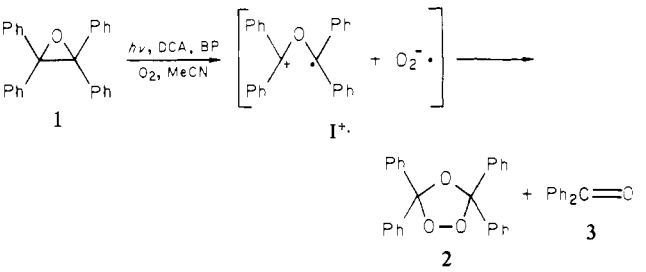
Received August 23, 1982

Olefins, acetylenes, and sulfides undergo electron-transfer photooxygenation with electron-deficient sensitizers in oxygen-saturated polar solvents.[2] Two general mechanisms have been identified: (1) addition of superoxide to the radical cation of the substrate to yield the product and (2) reaction of the radical cation with ground-state oxygen and subsequent reduction of the peroxy radical cation. ESR[2k] and laser flash[2i] spectroscopy have been used to identify reaction intermediates.

We have recently been interested in electron-transfer photooxygenation of substrates that exhibit low reactivity toward singlet oxygen. We now report that an epoxide can be converted in high yield to the corresponding ozonide by photooxygenation.[1] Also described is the first example of catalysis or cosensitization in an electron-transfer photooxygenation using a non-light-absorbing chemically unreactive aromatic hydrocarbon in conjunction with an electron-deficient photosensitizer.

Photooxygenation of tetraphenyloxirane (**1**) was carried out



in dry acetonitrile with 8×10^{-3} M **1** and 9×10^{-4} M 9,10-dicyanoanthracene (DCA). The solution was irradiated at 10 °C under oxygen with a 450-W medium-pressure mercury lamp using a $CuSO_4$-filter solution.[3] The reaction was monitored by HPLC and judged complete in 40 h.[4] Removal of the solvent and recrystallization of the residue from methanol at −25 °C gave 51% of pure ozonide **2**.[5] Concentration of the mother liquor and chromatography over silica gel gave an additional 13% of **2** and 25% of benzophenone (**3**).[7]

The slow rate of the reaction is not surprising as **1** does not measurably quench the fluorescence of DCA in acetonitrile.[8] However, *a dramatic enhancement of the rate of photooxygenation of* ***1*** *is observed in the presence of biphenyl* (*BP*). Addition of 8×10^{-4} M BP to the above reaction solution resulted in oxidation of **1** in 2 h with formation of 93% of **2** and 3% **3**.[9] In the presence of 8×10^{-3} M BP, the reaction was complete in only 10 min with similar yields of **2** and **3**. Analysis by HPLC indicated that BP was not appreciably consumed during the reaction. Control experiments have shown that no oxidation occurs in the absence of DCA and that **2** is not significantly decomposed to **3** under the reaction conditions. Further, epoxide **1** was not oxidized upon irradiation for 38 h with a 400-W high-pressure sodium lamp in an oxygenated acetonitrile solution containing rose bengal, indicating that $^1O_2$ is not involved in the reaction.

Griffin[10] and Arnold[11] have shown that electron-transfer reactions of aryl-substituted epoxides lead to C–C bond cleavage and formation of radical cations. A plausible mechanism for the formation of ozonide **2**, therefore, involves the addition of superoxide to radical cation $\mathbf{1}^{+\cdot}$ with formation of an intermediate biradical or zwitterion.[12] This intermediate could close to yield

(1) Presented at the IX IUPAC Symposium on Photochemistry, Pau, France, July 1982, Abstr. ST 15.

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(3) The 1-cm path length filter solution was prepared from 27 g of $CuSO_4 \cdot 5H_2O$, 30 g of $NaNO_2$, and 50 mL of concentrated NH_4OH diluted with water to 1000 mL.

(4) Irradiation times required for the photooxygenation of **1** in the absence of cosensitizer BP are quite variable (40–60 h).

(5) The mp (168–169 °C) and spectral properties of the isolated ozonide are identical with those of an authentic sample of **2** that was prepared by the method of Criegee and Korber.[6]

(6) Criegee, R.; Korber, H. *Chem. Ber.* **1971**, *104*, 1812.

(7) As 2 mol of **3** can result from **1**, yields of **3** are expressed as (mol of **3**/(2 × mol of **1**)) × 100.

(8) Foote has calculated that electron-transfer fluorescence quenching of DCA should be possible for substrates with oxidation potentials less than ~2 V vs. SCE.[2b] The lack of significant quenching by **1** and oxidation potentials of related compounds (*trans*-2,3-diphenyloxirane,[11] E^{ox} = 1.89 vs. $Ag/AgNO_3$ in acetonitrile; ~2.2 V vs. SCE) indicate that E^{ox} for **1** is >2 V.

(9) Yields were determined by HPLC using a C-18 reverse-phase column and elution with a gradient of 30–100% acetonitrile in water.

(10) Wong, J. P. K.; Fahmi, A. A.; Griffin, G. W.; Bhacca, N. S. *Tetrahedron* **1981**, *37*, 3345.

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(12) An alternative mechanism that cannot be ruled out at present involves the addition of $^3O_2$ to $\mathbf{1}^{+\cdot}$ with subsequent reduction of the peroxy radical cation by $O_2^{-\cdot}$, $DCA^{-\cdot}$, **1**, or BP.

0002-7863/83/1505-0663$01.50/0