ether, affording 504 mg of crude material containing some unreacted starting material. The desired thioether **16** was isolated by column chromatography on silica gel using 30% ether–benzene.

To a solution of 367 mg (1.07 mmol) of chromatographed thioether **16** in 5 ml of methylene chloride at 0° was added a solution of 190 mg (1.10 mmoles) of *m*-chloroperoxybenzoic acid in 5 ml of methylene chloride dropwise over 2.0 min. The solution was stirred for 2.0 hr at 0° and the solvent was removed by distillation at reduced pressure. The residue was taken up in ether and washed with two portions of saturated sodium bicarbonate solution to give the crude sulfoxide **17** as a white foam (276 mg).

This material was directly converted to the methylene lactone **10** according to the procedure of Trost and Salzmann.[14] A solution of 276 mg (0.77 mmol) of crude sulfoxide **17** in 8.0 ml of toluene was heated at reflux for 4.0 hr. The solution was cooled, diluted with ether, and washed with two portions of saturated sodium bicarbonate solution to afford 175 mg (98%) of crude product. Preparative thin layer chromatography on silica gel using 5% ether–benzene gave 4-deoxydamsin (R_f 0.39) as a white, crystalline solid: mp 108–110°; λ_{max} (melt) 3.38, 3.48, 5.70, 6.02, 7.85, 8.76, 10.04, 10.24, 10.60, 12.16 μ; δ_{TMS} ($CDCl_3$) 6.15 and 5.40 (doublets, J = 3.0 Hz, vinyl H's), 4.30 (d, J = 8.2 Hz, C-6 methine), 0.97 (d, J = 6.4 Hz, C-10 CH_3), 0.82 ppm (C-5 CH_3).

Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.65; H, 9.61.

Acknowledgments. Support for this project through a research grant (RO1 CA 11089) from the National Institutes of Health is gratefully acknowledged. We are indebted to Professor Tom Mabry and Mr. Eloy Rodríguez for a generous sample of *Ambrosia ambrosioides* extract.

Registry No.—**1**, 54798-48-0; **1** epoxide, 54798-49-1; **2**, 54798-50-4; **3**, 54798-51-5; *exo*-**4**, 54798-52-6; *endo*-**4**, 54798-53-7; *exo*-**5** epimer A, 54798-54-8; *exo*-**5** epimer B, 54798-55-9; *endo*-**5** epimer A, 54798-56-0; *endo*-**5** epimer B, 54798-65-1; **6** epimer A, 54910-30-4; **6** epimer B, 54809-86-8; **7** epimer A, 54798-63-9; **7** epimer B, 54798-64-0; **8**, 54798-58-2; **9**, 54798-60-6; **9** α-tosylate, 54798-61-7; (±)-**10**, 54798-59-3; (*S*)-**10**, 54831-46-8; **14**, 1216-42-8; **15**, 54798-57-1; **16**, 54798-62-8; *m*-chloroperoxybenzoic acid, 937-14-4; methyl bromoacetate, 96-32-2; *p*-toluenesulfonyl chloride, 98-59-9; thiophenol, 108-98-5.

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Use of the Azido Group in the Synthesis of 5′ Terminal Aminodeoxythymidine Oligonucleotides[1]

William S. Mungall, Geoffrey L. Greene, George A. Heavner, and Robert L. Letsinger*

Department of Chemistry and Department of Biochemistry and Molecular Biology, Northwestern University, Evanston, Illinois 60201

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Phosphoramidate analogs of oligonucleotides possess unique features which have interesting implications in nucleic acid chemistry.[2,3] In extending the synthetic methodology for this class of compounds we have explored the utility of the azido group as a synthon for a terminal amino group in an oligonucleotide. The formation of aminonucleosides by catalytic reduction of azidonucleosides is well known; representative examples include the preparation of 5′-amino-5′-deoxythymidine,[4] 2′-amino-2′-deoxyuridine,[5] and 5′-amino-2′,5′-dideoxyadenosine.[6] In addition, 5′-amino-5′-deoxythymidine 3′-phosphate and 3′-amino-3′-deoxythymidine 5′-phosphate have been obtained by catalytic hydrogenation of the corresponding azidonucleotides.[7]

As target compounds for study we selected di- and tetranucleotide analogs **2** and **4**. The synthetic scheme, outlined in Chart I, utilized the condensation procedure employed previously for preparation of some thymidylyl phosphoramidate analogs.[2]

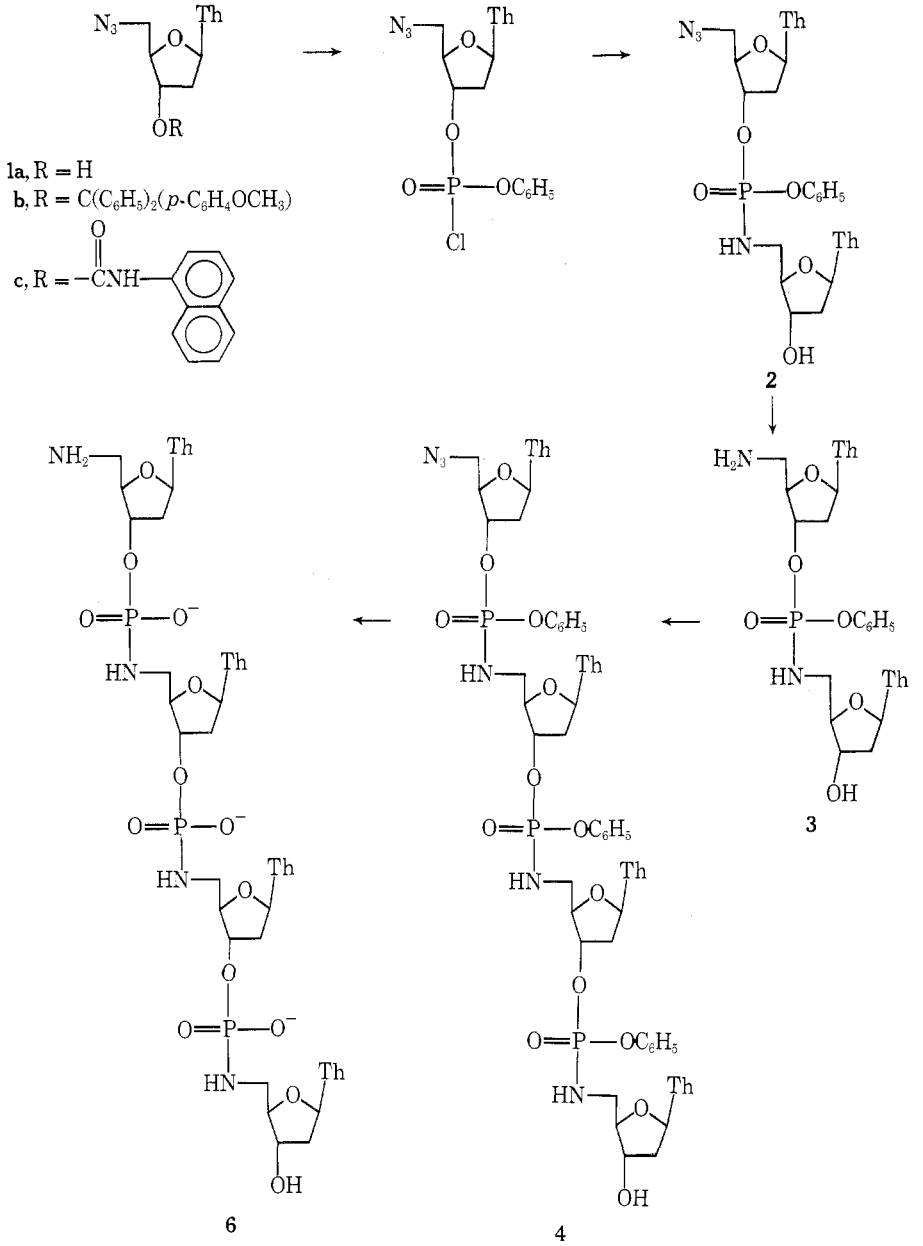
5′-Azido-5′-deoxythymidine (**1a**) reacted smoothly with phenyl phosphorodichloridate in pyridine to give an active phosphorylated intermediate, which on treatment with 5′-amino-5′-deoxythymidine afforded the desired azidodinucleoside phosphate analog, **2**, in good yield. In contrast to the facile catalytic hydrogenation of **1a**, however, the reduction of **2** with hydrogen over a platinum catalyst was sluggish. Under conditions where **1a** was converted to the aminodeoxythymidine in high yield (90% isolated), little reduction of **2** was achieved. When the time of reaction was increased fivefold (to 2.5 hr), **2** was partially reduced, and the desired amino derivative (**3**) was isolated in 54% yield.

Repetition of the synthetic sequence with **2** in place of **1a** and **3** in place of 5′-amino-5′-deoxythymidine gave compound **4**. This tetranucleotide derivative, however, proved to be resistant to hydrogenation with palladium and platinum catalysts under all conditions that were explored. The decrease in susceptibility to catalytic reduction for the series **1a**, **2**, **4** correlates with increasing steric bulk at the 3′-O position.

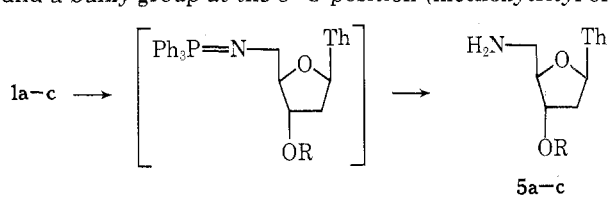
Of the other methods available for converting azides to amines, the most promising for application in the nucleotide field appeared to be that utilizing triphenylphosphine, first described by Staudinger and Hauser.[8] Thus, methyl and ethyl azide are converted by triphenylphosphine to phosphinimines, which are reported to hydrolyze on exposure to moisture to triphenylphosphine oxide and the corresponding amines. Other workers have used alkali (refluxing 2% alcoholic potassium hydroxide)[9] and strong acid (hot 40% hydrogen bromide in acetic acid)[10] to liberate substituted alkylamines from phosphinimines. The conversion of an azido sugar, tetraacetyl-β-D-glucosyl azide, to a triphenylphosphinimine has also been reported.[11]

Experiments with model nucleosides, 5′-azido-5′-deoxythymidine (**1a**), 3′-*O*-mono-*p*-methoxytrityl-5′-azido-5′-deoxythymidine (**1b**), and 3′-*O*-α-naphthylcarbamoyl-5′-azido-5′-deoxythymidine (**1c**), indeed showed that the triphenylphosphine hydrolytic sequence constitutes a convenient preparative technique for this class of compounds. The aminonucleoside (**5a–c**) was isolated in high yield

Chart I



(88–90%) in each case. The reactions are easily scaled up, and a bulky group at the 3′-O position (methoxytrityl or α-



napthylcarbamoyl) does not interfere. In contrast to the phosphinimines derived from the simple alkyl azides, the intermediates obtained from the azidonucleosides are relatively stable in water. They hydrolyze cleanly to the aminonucleosides, however, on treatment with ammonium hydroxide or aqueous sodium hydroxide at room temperature. Indeed, the amine can be obtained directly by treating the azide with a solution containing both triphenylphosphine and ammonium hydroxide in pyridine.

Treatment of compound **4** with triphenylphosphine in pyridine, followed by hydrolysis with aqueous sodium hydroxide, yielded the aminotetranucleoside triphosphate, **6**, with no observable products of side reactions. Furthermore, **2** could be converted to **3** by the action of triphenylphosphine and ammonium hydroxide, demonstrating that reduction of a terminal azido function can be achieved under conditions where a phenoxy group masking an internucleotide phosphoramidate link is stable. These experiments therefore indicate that a procedure utilizing a terminal azido group and reduction of the azide with triphenylphosphine offers an attractive route for synthesis of an oligonucleotide terminated with an amino group.

Experimental Section

The equipment and general procedures were the same as described in ref 1 (part XIX). The chromatographic solvents were: A, *i*-C_3H_7OH–NH_4OH–H_2O (7:1:2); F, *n*-C_3H_7OH–NH_4OH–H_2O (55:10:35). Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Ill.

Phenyl Ester of 5′-Azido-5′-deoxythymidylyl-(3′–5′)-5′-amino-5′-deoxythymidine (2). Dry 5′-azido-5′-deoxythymidine (801 mg, 3 mmol) in dioxane (30 ml) was stirred with phenyl phosphorodichloridate (0.48 ml, 3 mmol) and pyridine (0.48 ml, 6 mmol) for 48 hr at room temperature. Triethylamine (0.84 ml, 6 mmol) and a solution of 5′-amino-5′-deoxythymidine (850 mg, 3.7 mmol) in dioxane (240 ml) were then added. The mixture was stirred for 30 min and then cooled with an ice bath. Aqueous sodi-

Table I
Chromatographic and Electrophoretic Values[a]

Compd	R_f (solvent A)	R_f (solvent F)	R_m[b]
$d(N_3)T$	0.7	0.9	−0.1
$d(N_3)Tp$	0.2	0.7	+1.0
$d(N_3)Tp(NH)T$	0.4	0.7	+0.3
$d(N_3)Tp(NH)Tp(NH)Tp(NH)T$	0.03	0.4	+0.7
$d(NH_2)T$	0.5	0.7	−0.7
$d(NH_2)Tp$	0.09	0.5	+0.45
$d(NH_2)Tp(NH)T$	0.1	0.6	−0.1
$d(NH_2)Tp(NH)Tp(NH)Tp(NH)T$	0.02	0.3	+0.5
dT	0.6	0.8	−0.1
dTp	0.1	0.5	+1.0
dTp(NH)T	0.3	0.6	+0.35
dTp(NH)Tp(NH)Tp(NH)T	0.02	0.4	+0.7

[a] Other identifying characteristics are: (1) all amino derivatives give a positive ninhydrin test; (2) on silica gel TLC in ethyl acetate R_f for dT is 0.1; none of the 5′-amino derivatives or the compounds bearing charged phosphoryl groups moved on TLC under these conditions. [b] Electrophoretic migration relative to d_pT at pH 7.2.

um hydroxide (10 ml, 0.5 *M*) was added, and the mixture was filtered immediately to remove the precipitated salts. The filtrate was concentrated to a syrup at reduced pressure, and, after addition of water (20 ml), the mixture was extracted twice with ethyl acetate (300, 100 ml). The organic extract was dried over sodium sulfate, evaporated at reduced pressure, and chromatographed on a silica gel column (4 × 50 cm) with 1.5 l. of ethyl acetate [which removed azidodeoxythymidine, 203 mg, 0.76 mmol, R_f (EtOAc) 0.37] followed by 1 l. of tetrahydrofuran. Concentration of the fractions and precipitation with hexane afforded 1.41 g [96% yield based on unrecovered $d(N_3)T$; 71% based on initial $d(N_3)T$] of **2**: mp 120–123° (softening at 115°); λ_{max} 264 nm (ϵ 18,000); λ_{min} 234 nm (ϵ 4500); principal infrared bands at 3.2, 4.8, 5.9, 6.8, and 7.9 μ; homogeneous on TLC, R_f (EtOAc) 0.04; R_f (THF) 0.55.

Anal. Calcd for $C_{26}H_{31}N_8O_{10}P$: C, 48.30; H, 4.83; N, 17.33. Found: C, 48.29; H, 4.89; N, 16.76.

For further characterization this product was hydrolyzed with 0.1 *M* aqueous sodium hydroxide (6 hr, 23°). A single nucleotidic product was observed on paper chromatography in solvent A (R_f 0.40). Elution with water and lyophilization afforded $d(N_3)T_p(NH)T$ as a white powder, R_f (F) 0.68 and R_m 0.29. This product hydrolyzed quantitatively to $d(N_3)T_p$ and $d(NH_2)T$ (**5a**) on treatment with aqueous acetic acid. In addition it was quantitatively cleaved by snake venom phosphodiesterase and by spleen phosphodiesterase under the standard conditions to give $d(N_3)T$ + $d(NH_2)T$ and $d(N_3)T_p$ + $d(NH_2)T$, respectively (see Table I for properties of the hydrolytic products).

Catalytic Reduction of Azide 2 to Amine 3. A solution of azide **2** (500 mg, 0.77 mmol) in 100 ml of absolute ethanol was shaken with platinum oxide catalyst (150 mg) for 1.5 hr under 30 psi pressure of hydrogen. An additional 100 mg of the catalyst was added and the hydrogenation was continued for another 1 hr. Analysis by TLC showed two spots, attributable to **3** [R_f (THF) 0.1, positive ninhydrin test] and unreduced starting material [R_f (THF) 0.7]. Filtration, concentration, and chromatography on silica gel (2 × 30 cm). Elution successively with tetrahydrofuran (500 ml), 1:9 ethanol–tetrahydrofuran (100 ml), and 3:7 ethanol–tetrahydrofuran (200 ml) afforded 258 mg (54%) of **3** (precipitated by addition of hexane to fractions homogeneous by TLC): mp 135–138° with softening at 128°; λ_{max} 265 nm (ϵ 18,000); λ_{min} 234 nm (ϵ 4100); principal infrared bands at 3.0, 3.2, 5.9, 6.8, and 7.9 μ; R_m −0.4 relative to dpT; R_f (F) 0.8; R_f (A) 0.5.

Anal. Calcd for $C_{26}H_{33}N_6O_{10}P \cdot H_2O$: C, 48.90; H, 5.52; N, 13.16. Found: C, 48.70; H, 5.34; N, 12.92.

Hydrolysis of **3** with 0.1 *M* sodium hydroxide in 50% aqueous dioxane (6 hr at room temperature), neutralization, and chromatography on paper with solvent A yielded a single nucleotidic product, $d(NH_2)Tp(NH)T$, identical in electrophoretic and chromatographic properties (Table I) with $d(NH_2)Tp$-(NH)T prepared previously by a different route.[2]

$d(N_3)Tp_{(Ph)}(NH)Tp_{(Ph)}(NH)Tp_{(Ph)}(NH)T$ (4). Compound **2** (200 mg, 0.31 mmol), dried by evaporation of three 1-ml portions of pyridine, was dissolved in dioxane (6 ml) and treated with phenyl phosphorodichloridate (0.050 ml, 0.31 mmol) and pyridine (0.050 ml, 0.62 mmol) for 65 hr. Triethylamine (0.087 ml, 0.62 mmol) and a solution of **3** (120 mg, 0.21 mmol) in 40 ml of dioxane were added and stirring was continued for 2 hr. Aqueous 0.5 *M* sodium hydroxide (1 ml) was added (15 min) and the resulting solution was concentrated to a syrup at reduced pressure. Chromatography on a silica gel column (3 × 32 cm) with ethyl acetate (100 ml), ethyl acetate–tetrahydrofuran (1:1, 250 ml; 1:3, 250 ml), and tetrahydrofuran (500 ml), followed by precipitation by addition of hexane to the fractions, afforded three substances insoluble in hexane: unreacted **2** (11 mg, 6%), compound **4** (149 mg, 44%), and a product tentatively identified as phenyl-phosphorylated **2** [$d(N_3)Tp_{(Ph)}(NH)Tp_{(Ph)}$; R_m 0.21 relative to d_pT on paper electrophoresis at pH 7.2]. An analytical sample of **4**, obtained by rechromatography and reprecipitation with hexane, melted at 144–148° (softening at 141°).

Anal. Calcd for $C_{58}H_{67}N_{14}P_3O_{22} \cdot H_2O$: C, 48.94; H, 4.74; N, 13.81. Found: C, 49.10; H, 4.84; N, 13.22.

Characterization of 4. The phenyl protecting groups were removed from **4** by treatment with 0.1 *M* aqueous sodium hydroxide for 6 hr in the usual manner.[2] After neutralization with dilute acid, paper chromatography in solvent F showed a single nucleotidic product (R_f 0.35). This product, $d(N_3)T_p(NH)T_p(NH)T_p(NH)T$, was eluted with water and isolated by lyophilization. In preparation for hydrolytic degradation it was further purified by rechromatography on paper with solvent A and by paper electrophoresis (pH 7.2; R_m 0.7 relative to d_pT). This material was hydrolyzed by aqueous acetic acid and by snake venom phosphodiesterase.[2] The products were separated by paper chromatography in solvent A, and the relative quantities were determined by eluting the materials from the paper and measuring the absorbance at 260 nm. In conformity with the assigned structure, the substance was completely degraded in each case. The venom degradation afforded two products, $d(N_3)T$ and $d(NH_2)T$ (1.03 and 3.3 optical density units, respectively), and the acid hydrolysis yielded $d(N_3)T$, $d(NH)T_p$, and $d(NH_2)T$ (1.4:2.1:1.2 optical density units, respectively). These substances were characterized by their electrophoretic and chromatographic behavior (Table I).

5′-Amino-5′-deoxythymidine (5a). 5′-Azido-5′-deoxythymidine (5.00 g, 18.7 mmol) and triphenylphosphine (8.00 g, 30.5 mmol) were dissolved in 15 ml of pyridine and kept at room temperature for 1 hr. Concentrated ammonium hydroxide was then added and the solution was allowed to stand for an additional 2 hr. Pyridine was removed at reduced pressure, water was added, and triphenylphosphine and triphenylphosphine oxide were removed by filtration. The filtrate was extracted with benzene and with ether to remove residual triphenylphosphine and then concentrated to dryness. Recrystallization of the solid residue from ethanol afforded 4.1 g (90%) of 5′-amino-5′-deoxythymidine, mp 178–180°, mmp with a sample prepared by catalytic hydrogenation, 178–180°. The chromatographic properties [R_f (CH_3OH) 0.26] and the infrared spectrum were identical with those for the authentic sample.

5′-Amino-5′-deoxy-3′-*O*-naphthylcarbamoylthymidine (5c). Naphthyl isocyanate (1.4 ml, 10 mmol) was added to 5′-azido-5′-deoxythymidine (0.53 g, 2 mmol, dried by distillation of anhydrous pyridine) in pyridine (20 ml). After 1 hr the product was precipitated by addition of 1 l. of hexane. The precipitate was collected by centrifugation, washed with hexane, redissolved in pyridine (8 ml), and again precipitated with hexane (400 ml). The product (**1c**) weighed 0.85 g (98%); R_f (THF) 0.63; principal infrared bands at 3.0, 3.25, 4.75, 5.9, and 6.5 μ.

For reduction of the azido function, **1c** (0.217 g, 0.5 mmol) was treated with triphenylphosphine (0.26 g, 1 mmol) in pyridine (1 ml) for 1 hr, followed by addition of concentrated ammonium hydroxide (0.4 ml). After 8 hr the solution was concentrated to a gum and anhydrous pyridine was evaporated twice from the residue to remove water. The gum was then taken up in a small volume of pyridine and added slowly to 1:1 hexane–cyclohexane (350 ml). The resulting white precipitate was collected by centrifugation, washed, and crystallized from ethanol to give 0.184 g (88% from **1c**) of **5c**, mp 207–210°, R_f (THF) 0.50, R_f (EtOAc) 0.03. An analytical sample obtained by recrystallization from ethanol melted at 211–212°; λ_{max} (EtOH) 270 nm (ϵ 13,000), λ_{min} 244 nm (ϵ 6400); principal infrared bands at 2.9, 3.25, 5.8, 6.0, 6.45, and 8.15 μ.

Anal. Calcd for $C_{21}H_{22}N_4O_5$: C, 61.45; H, 5.40; N, 13.65. Found: C, 61.43; H, 5.45; N, 13.55.

5′-Amino-5′-deoxy-3′-*O*-mono-*p*-methoxytritylthymidine (5b). 5′-Azido-5′-deoxythymidine was converted to the 3′-*O*-mono-*p*-methoxytrityl ether by reaction with mono-*p*-methoxytrityl

chloride essentially as described for preparation of related nucleoside derivatives.[12] Compound **1b** was obtained in 85% yield as a white solid melting at 93–98°; λ_{max} (EtOH) 266 nm (ϵ 11,500), λ_{min} 250 nm (ϵ 9650).

Anal. Calcd for $C_{30}H_{29}N_5O_5$: C, 66.78; H, 5.42; N, 12.98. Found: C, 66.35; H, 5.27; N, 13.28.

Compound **1b** (0.27 g, 0.5 mmol) and triphenylphosphine (0.26 g, 1 mmol) were dissolved in pyridine (0.6 ml) at 0°. Concentrated ammonium hydroxide (0.4 ml) was added and the solution was allowed to warm to room temperature. After 2 hr TLC revealed that the azide had reacted completely but the phosphinimine had only partially hydrolyzed to the amine [R_f (CH_2Cl_2–THF 1:1) 0.35 for **1b** and 0.20 for the phosphinimine]. Additional pyridine–ammonia (1 ml, 6:4 v/v) was added and the mixture was allowed to stand overnight, at which time the reaction was complete by the TLC test. Work-up as described for **1c** yielded 0.23 g (88%) of compound **5b**. This sample [R_f (EtOAc) 0.01] contained traces of material with R_f 0 (ninhydrin positive) and R_f 0.47 (positive to perchloric acid spray). Thick layer chromatography on silica gel yielded a pure sample (softened at 100°, completely melted at 114°), λ_{max} (EtOH) 265 nm (ϵ 11,100), λ_{min} 250 nm (ϵ 9190).

Anal. Calcd for $C_{30}H_{31}N_3O_5$: C, 70.16; H, 6.08; N, 8.18. Found: C, 69.89; H, 5.82; N, 8.15.

$d(NH_2)T_p(NH)T_p(NH)T_p(NH)T$ (6). A solution of **4** (16 mg, 0.015 mmol) and triphenylphosphine (43 mg, 0.16 mmol) in pyridine (0.5 ml) was stirred at 25° for 1.5 hr, mixed with water (0.5 ml), and stirred for an additional 2 hr. The solvent was evaporated under reduced pressure, aqueous sodium hydroxide (1.0 ml, 0.2 *M*) was added, and the mixture was stirred overnight. Following extraction with methylene chloride (5 × 2 ml) a small portion of the aqueous layer was analyzed by paper electrophoresis at pH 7.2. A strong spot was observed under ultraviolet light at R_m −0.51 (relative to d_pT), and it was ninhydrin positive; the only other nucleotidic material appeared as a very faint spot (ninhydrin negative) at R_m 0.73, corresponding to a trace of unreacted **4**. The reaction product was separated from the major portion of the solution by chromatography on paper with solvent F. Elution with water, conversion to the triethylammonium salt, and lyophilization afforded 18 mg of **6**, R_f (F) 0.33. Hydrolysis of an aliquot with 80% aqueous acetic acid (15 min on steam bath) yielded $d(NH_2)T$ and $d(NH_2)T_p$ (see Table I for properties) in a ratio of 1:2.8.

Reduction of Azide 2 to Amine 3 with Triphenylphosphine. Compound **2** (10 mg, 0.015 mmol) was added to a solution of triphenylphosphine (10 mg, 0.04 mmol) in pyridine (0.1 ml) and 50% saturated methanolic ammonia (0.1 ml). After 72 hr the solution was concentrated under reduced pressure, and the residue was dissolved in methanol and spotted on Whatman 3MM paper. Development in solvent A yielded **3** as a spot at R_f 0.56 (visualized under uv light, ninhydrin positive). The product was eluted from the paper with tetrahydrofuran and was precipitated from the tetrahydrofuran with hexane. On drying to constant weight, 7.5 mg (78%) of **3** was obtained, mp 139–141° (with softening at 130°). It was identical with **3** (prepared independently by catalytic reduction) on TLC [R_f (THF) 0.12], paper chromatography with solvent A, and paper electrophoresis (R_m −0.4 relative to d_pT, pH 7.2, 0.05 *M* sodium phosphate buffer).

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Registry No.—**1a,** 19316-85-9; **1b,** 54814-97-0; **1c,** 54814-98-1; **2,** 54814-99-2; **2** phenyl phosphorylated, 54815-00-8; **3,** 54815-01-9; **4,** 54815-02-0; **5a,** 25152-20-9; **5b,** 54815-03-1; **5c,** 54815-04-2; **6,** 54815-05-3; phenyl phosphorodichloridate, 770-12-7; naphthyl isocyanate, 86-84-0; mono-*p*-methoxytrityl chloride, 14470-28-1; triphenylphosphine, 603-35-0.

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Dehydration of *erythro*- and *threo*-1,2-Diphenyl-1-propanol with Iodine, *p*-Toluenesulfonic Acid, and Methyltriphenoxyphosphonium Iodide

Wilkins Reeve* and Ruth M. Doherty

Department of Chemistry, University of Maryland, College Park, Maryland 20742

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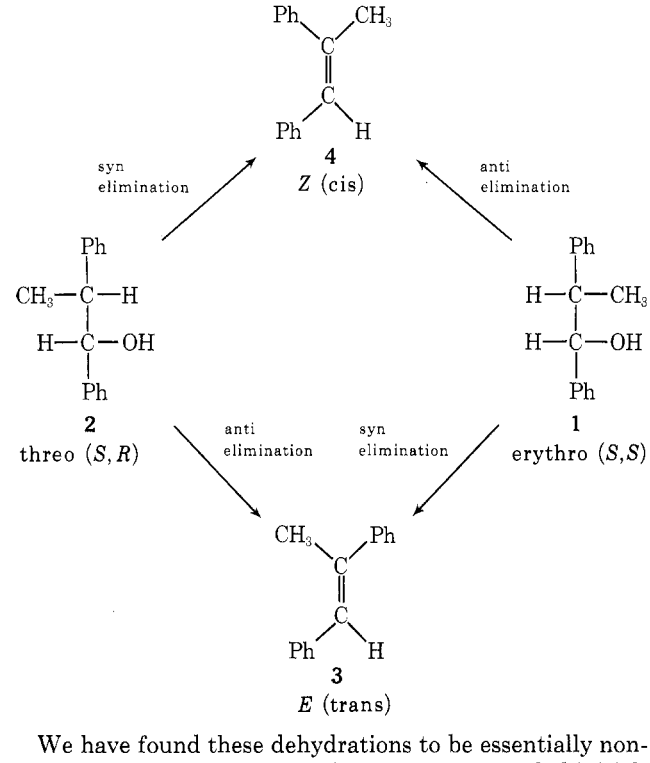
Iodine has long been used as a catalyst for the dehydration of secondary alcohols,[1,2] including diacetone alcohol,[1,3] and tertiary alcohols,[1,2] including pinacols.[1,4] Little is known about why iodine has this remarkable catalytic activity and nothing is known about the stereochemistry of iodine-catalyzed dehydrations. We have studied the dehydration of the erythro (**1**) and threo (**2**) isomers of 1,2-diphenyl-1-propanol to determine the stereochemistry of the reaction.



We have found these dehydrations to be essentially nonstereospecific. In both cases the reaction proceeded initially with about 55% anti-periplanar elimination. This was followed by equilibration to the equilibrium mixture consisting of 72% *E*- (**3**) and 28% *Z*-α-methylstilbene (**4**). The threo alcohol (**2**) dehydrated more rapidly than its erythro isomer.

The *p*-toluenesulfonic acid (PTSA) catalyzed dehydration of **1** and **2** in refluxing *p*-xylene was also found to proceed initially in a nonstereospecific manner followed by equilibration of **3** and **4** on longer heating. As with the iodine-catalyzed reaction, the threo alcohol dehydrated more rapidly than the erythro isomer. With both iodine and PTSA our results are consistent with the formation with a common intermediate carbonium ion, but are insufficient