high-pressure lamp of the same solution furthermore gives rise to an esr signal (g = 2.005). However, further studies using the combined esr and optical flash technique[12] are needed for a definitive assignment.

A radical-chain mechanism, found recently for the sensitized dimerization of 1,1-bis(*p*-dimethylaminophenyl)ethylene[13] is unlikely on the basis of the quantum yield for formation of **4** which is less than 10^{-1}.

The same products, **3** and **4**, are formed when the acetonitrile solution is irradiated at 254 nm (low-pressure mercury vapor lamp). At this wavelength olefin **2** absorbs most of the light ($\epsilon(\mathbf{1}):\epsilon(\mathbf{2})$ = 1:3), whereas, upon irradiation with the medium-pressure mercury vapor lamp through Pyrex mostly **1** is excited ($\epsilon(\mathbf{1}):\epsilon(\mathbf{2})$ = 7:1 at 302 nm and 1:1 at 313 nm). The absorption spectrum, at long wavelengths, shows no evidence for complex formation between ground state molecules; however, a weak complex might not be detected.[14]

Formation of **4** is not restricted to sensitization by **1**; methyl *o*-cyanobenzoate or dimethyl terephthalate can also be used.[15] A thorough investigation of the efficiency of the reaction under various conditions is in progress.

Upon irradiation of **1** and **2** in methanol and 2-propanol we found formation of 2,2-diphenylethyl methyl ether (**7**) and 2,2-diphenylethyl isopropyl ether (**8**), respectively, arising from nucleophilic attack of the alcohol on **6**. In both solvents formation of **4** was completely suppressed. The structures of **7** and **8** (after isolation by chromatography on silica gel) were proven by nmr, using spin decoupling and, in the case of **7**, by comparison with an authentic sample.[16]

Proton transfer from the solvent to an excited state of **2** cannot be important in these reactions because formation of the most stable carbonium ion, at the carbon atom bearing the phenyl groups, would lead to other products.[17] If a radical process were involved a carbon–hydrogen bond of the alcohol would be broken rather than the oxygen–hydrogen bond which has the higher bond dissociation energy. Irradiation of **2** in 2-propanol has been reported to yield the three possible coupling products of 1,1-diphenylethyl- and dimethylcarbinol radicals.[18] None of these products was formed in detectable amounts when **1** was present; this means that in our experiments either practically all the light is absorbed by the ester **1** (as stated above) forming the exciplex or that excited **2** leads to formation of **6** in the presence of **1** at a rate faster than hydrogen abstraction from the solvent.

Very little oxetane **3** was formed in the methanol experiment, whereas irradiation in 2-propanol produced appreciable amounts of **3** (**3**:**8** = 1:3.2) besides small quantities of unidentified products. This sensitivity of product distribution to solvent polarity convinces us that the cation radical of 1,1-diphenylethylene (**6**) is the reactive species in reactions leading to **4**, **7**, and **8** and its formation by dissociation of the exciplex is the product-determining step. The solvent polarity, as expressed by the Kirkwood–Onsager parameter (Ω),[19] increases in the order 2-propanol < acetonitrile < methanol. The relative yield of **3** decreases in the same order, whereas the yield of the products arising from **6** increases.

In conclusion we wish to point out that this reaction provides a convenient procedure to achieve anti-Markovnikov addition of alcohols to olefins which can presumably be extended to other systems. Furthermore, the addition of other nucleophiles to photochemically generated cation radicals would make this type of reaction of more general synthetic utility.

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(12) J. T. Warden and J. R. Bolton, *J. Amer. Chem. Soc.*, **94**, 4351 (1972).
(13) A. Ledwith, *Accounts Chem. Res.*, **5**, 133 (1972).
(14) C. Lewis and W. R. Ware, *Chem. Phys. Lett.*, **15**, 290 (1972).
(15) Methyl benzoate, benzophenone, and Methylene Blue are essentially unreactive.
(16) W. A. Bonner and F. D. Mango, *J. Org. Chem.*, **29**, 434 (1964).
(17) P. J. Kropp, *Pure Appl. Chem.*, **24**, 585 (1970).
(18) H. M. Rosenberg and P. Servé, *J. Amer. Chem. Soc.*, **92**, 4746 (1970).
(19) (a) J. G. Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934); **7**, 911 (1939); (b) L. Onsager, *J. Amer. Chem. Soc.*, **58**, 1486 (1936); (c) J. Powling and H. J. Bernstein, *ibid.*, **73**, 1815, 4353 (1951).
(20) Alfred P. Sloan Fellow, 1972–1974.

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Synthesis and Absolute Configuration of (+)-5-(4′,5′-Dihydroxypentyl)uracil from *Bacillus subtilis* Phage SP-15 Deoxyribonucleic Acid

Sir:

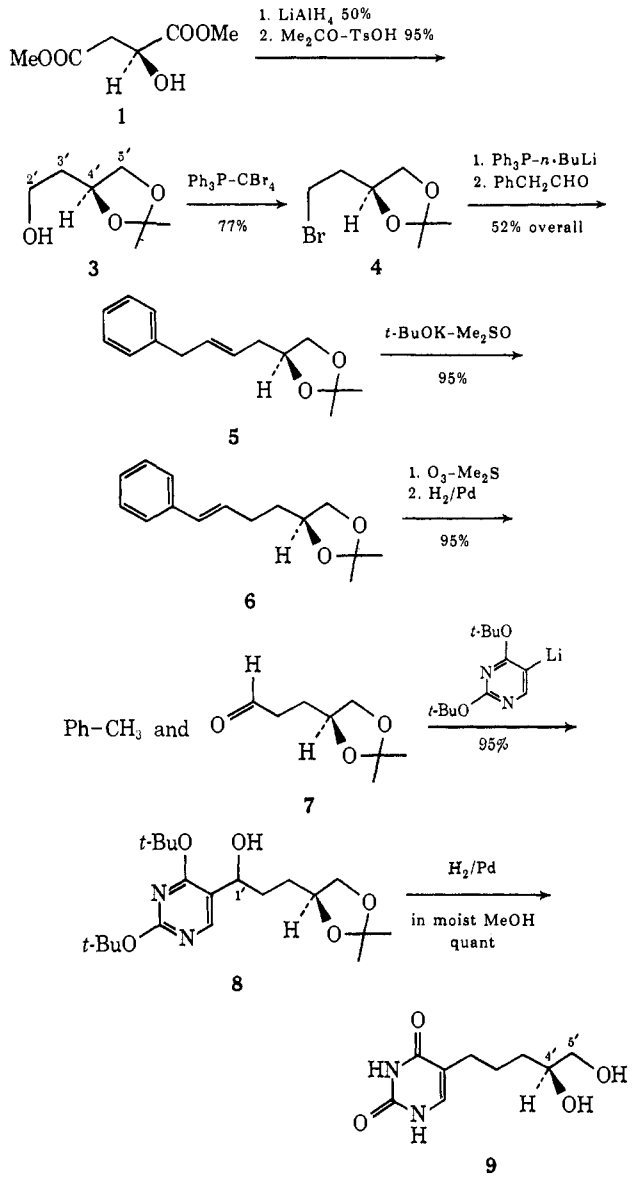
In the following we report the synthesis of (+)-5-(4′,5′-dihydroxypentyl)uracil, the modified base which replaces thymine in bacteriophage SP-15 deoxyribonucleic acid (DNA) of *Bacillus subtilis*.[1] The synthesis allows one to assign an *S* configuration to this compound, which is the sole DNA base known so far to contain a chiral side chain. We also describe a C_1-homologation sequence which can be carried out under the presence of acid-labile functionalities.

(*S*)-(−)-Malic acid was methylated with hydrogen chloride in methanol to give the dimethyl ester **1**, which was reduced to 1,2,4-butanetriol (**2**)[2] with lithium alminum hydride in tetrahydrofuran (50%). Treatment of triol **2** with acetone and *p*-toluenesulfonic acid (Scheme I) gave a single acetonide (95%), to which the five-membered structure **3** was assigned from nmr: 2′-H at 3.75 ppm (t, J = 6.0 Hz), 3′-H at 1.81 ppm (d of t, J = 5.5 and 6.0 Hz). Namely, the triplet nature of the 3.75-ppm signal can only be accounted for by a freely rotating primary alcohol group attached to a methylene (C-3′).

The triol acetonide **3** was brominated to **4** (77%) under mild neutral conditions by the addition of triphenylphosphine (1 mol equiv) in dichloromethane to a mixture of acetonide **3** and carbon tetrabromide[3] (1:1.5 equiv) in the same solvent; triphenylphosphine

(1) J. Marmur, C. Brandon, S. Neubort, M. Ehrlich, M. Mandel, and J. Konvicka, *Nature (London), New Biol.*, **239**, 68 (1972); C. Brandon, P. M. Gallop, J. Marmur, H. Hayashi, and K. Nakanishi, *ibid.*, **239**, 70 (1972).
(2) Analytical and spectroscopic data of all synthetic compounds were in agreement with their structures.
(3) F. Ramirez, N. B. Desai, and N. McKelvie, *J. Amer. Chem. Soc.*, **84**, 1745 (1962); D. Brett, I. M. Downie, J. B. Lee, and M. F. S. Matough, *Chem. Ind (London)*, 1017 (1969); R. G. Weiss and E. I. Snyder, *J. Org. Chem.*, 36, 403 (1971); J. S. McKennis, L. Brener, J. S. Ward, and R. Pettit, *J. Amer. Chem. Soc.*, **93**, 4957 (1971).

Scheme I[a]



[a] Numberings in structures correspond to those in base **9**; the yields refer to those after purification.

was added *slowly* through a capillary so as to avoid the presence of an excess and hence formation of triphenylphosphine dibromide. Compound **4** was converted to the triphenylphosphine salt (100°, sealed tube in ether; 87%), which was then allowed to react with *n*-butyllithium in tetrahydrofuran to give the phosphorane. Dropwise addition of phenylacetaldehyde at −70° gave the homoconjugated *E* compound **5** containing a trace of the *Z* isomer (nmr evidence) (60%).

Shaking of the unseparated *E* and *Z* mixture of **5** for 2 hr at room temperature in dimethyl sulfoxide[4] containing 1.3 equiv of potassium *tert*-butoxide isomerized the double bond and yielded the *trans*-styrene **6** (95%): uv (hexane) 251 nm (ε 18,500); CD (hexane) $\Delta\epsilon_{250}$ +1.87.

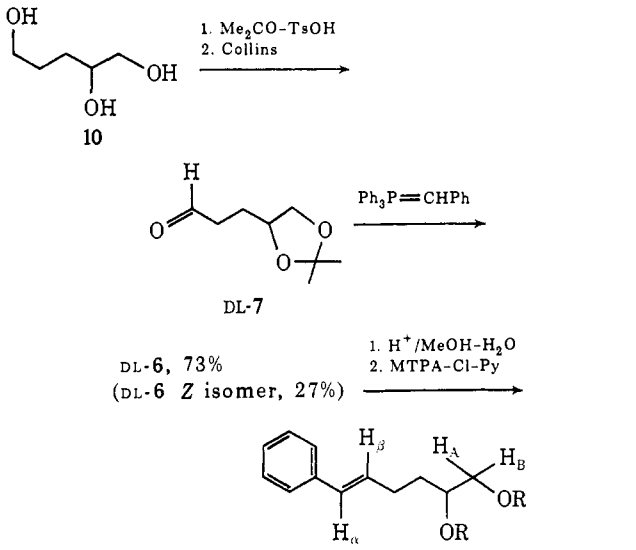
Ozonization of **6** in dry methanol followed by dimethyl sulfide reduction of the ozonide[5] gave a mixture of aldehyde **7** and benzaldehyde; the latter was removed as toluene by direct hydrogenolysis of the mixture with palladium black in dry methanol (yield of aldehyde **7**, 95%). The sequence leading from bromide **4** to aldehyde **7** (*ca.* 50% overall yield) constitutes a C_1 homologation[6] under nonacidic conditions; since the styrene moiety (potential aldehyde) in **6** is stable to acids and bases it allows possibilities for further modification of functionalities at this stage if required.[7]

The condensation product **8**, a diastereomeric mixture at C-1′ (nmr), was obtained in 95% yield by mixing tetrahydrofuran solutions of aldehyde **7** and 1.1 equiv of 5-lithio-2,4-di-*tert*-butoxypyrimidine[8] at −70°. Finally, hydrogenolysis (18 hr at room temperature) with palladium black in moist methanol removed the benzylic hydroxyl and protecting groups[9] in quantitative yield and gave (*S*)-(+)-5-(4′,5′-dihydroxypentyl)-uracil (**9**): mp 225–226°; uv (in H_2O) 207 (ε 9500), 265 nm (ε 7700); CD (H_2O) $\Delta\epsilon_{265}$ +0.5.

The optical purity of base **9** was checked at the stage of styrenoid **6** since the insolubility of base **9** in nonpolar solvents precluded usage of chiral nmr shift reagents, and moreover, it was not simple to selectively prepare diastereomeric derivatives at C-4′ in **9**.

The DL-acetonide aldehyde **7**, prepared from DL-1,2,5-pentanetriol[10] in two steps (62% overall yield, Scheme II), was allowed to react with triphenylbenzyl-

Scheme II



11, R = H
12, R = (+)-MTPA diastereomers I, II (1:1)

idenephosphorane to give 73% DL-**6** and 27% of its *Z* isomer (glc separation, *ca.* 70% yield). The DL-ace-

(4) J. Ugelstad, B. Jenssen, and P. C. Mörk, *Acta Chem. Scand.*, **16**, 323 (1962).

(5) J. J. Pappas, W. P. Keaveney, E. Gancher, and M. Berger, *Tetrahedron Lett.*, 4273 (1966).

(6) Other recent C_1 homologations: A. I. Meyers, A. Nabega, H. W. Adickes, I. R. Politzer, G. R. Malone, A. C. Kenelsky, R. L. Nolen, and R. C. Portnoy, *J. Org. Chem.*, 38, 36 (1973); H. M. Walborsky, W. H. Morrison III, and G. E. Niznik, *J. Amer. Chem. Soc.*, **92**, 6675 (1970); E. J. Corey and D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **4**, 1075 (1965); D. Seebach, *Synthesis*, **1**, 17 (1969); G. Wittig, W. Böll, and K. H. Krück, *Chem. Ber.*, **95**, 2514 (1962).

(7) For example, a sugar is probably attached to the α-glycol group of base **9** in the original DNA molecule (private communication from Professor J. Marmur). Intermediate **6** would be suited for synthesis of such a glycosidic nucleoside.

(8) D. M. Brown, M. G. Burdon, and R. P. Slatcher, *J. Chem. Soc. C*, 1051 (1968).

(9) Removal of acetonide groups in compounds such as **3**–**6** requires acid conditions. The contrasting facile cleavage of the acetonide in **8** in moist methanol is presumably due to an acid catalytic effect of the uracil moiety.

(10) C. L. Wilson, *J. Chem. Soc.*, 48 (1945).

tonide **6** was hydrolyzed to the α-glycol (quantitative) **11**, but the two antipodal glycols could not be distinguished by nmr (^1H and ^{13}C) after addition of the chiral shift reagents tris[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]europium(III)[11a] and tris-[3-(heptafluoropropylhydroxymethylene)-*d*-camphorato]europium(III).[11b] The DL-glycol **11** was therefore allowed to react with (+)-α-methoxy-α-trifluoromethylphenylacetyl (MTPA) chloride[12] to give a (1:1) mixture of the two diastereomers **12** which were distinguishable by the following sets of nmr proton peaks (but not by ^{19}F): diastereomer I, H_A δ 4.30 (d of d, J = 12.5 and 5.0 Hz), H_B 4.60 (d of d, J = 12.5 and 3.0 Hz), H_β 6.07 (d of t, J = 16 and 6.5 Hz), H_α 6.37 (d, J = 16 Hz); diastereomer II, H_A δ 4.28 (d of d, J = 12 and 5.0 Hz), H_B 4.68 (d of d, J = 12 and 3.0 Hz), H_β 6.02 (d of t, J = 16 and 6.5 Hz), H_α 6.31 (d, J = 16 Hz).

The optically active specimen **6** from (*S*)-(−)-malic acid was similarly hydrolyzed and converted to the di-MTPA ester corresponding to **12**. The ester showed only one set of nmr peaks corresponding to those of diastereomer I. As it is inconceivable that partial racemization should occur in steps leading from **6** to **9** (Scheme I), the final product **9** can be regarded as being optically pure.

The small amount of natural base isolated previously[1] exhibited a positive Cotton effect at 264 nm as in the case of synthetic (+)-**9**, and the physical properties of natural and synthetic specimens were identical. The full structure of the natural base is thus established. The side-chain C-4′ configuration is opposite to that at C-4′ of D-ribose, and therefore the unique side chain is presumably not derived from D-ribose but from glutamic acid.

Acknowledgment. Support from National Institutes of Health Grant No. CA 11572 and the Hoffman-La Roche Foundation is acknowledged.

(11) (a) H. L. Goering, J. N. Eikenberry, and G. S. Koermer, *J. Amer. Chem. Soc.*, **93**, 5913 (1971); (b) R. R. Fraser, M. A. Petit, and J. K. Saunders *Chem. Commun.*, 1450 (1971).

(12) J. A. Dale, D. L. Dull, and H. S. Mosher, *J. Org. Chem.*, **34**, 2543 (1969).

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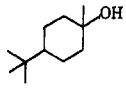
Thermal Decomposition of *N*-Chlorosulfonylurethanes. The Conversion of Alcohols to Amines

Sir:

There is a series of thermal reactions, ROCOZ → RZ + CO_2,[1-5] which serve in effect to convert alcohols to other functionalities. Such a reaction with Z = N< should be of considerable synthetic importance but has not been realized heretofore. We have found that the *N*-chlorosulfonylurethans of tertiary alcohols and of other alcohols, ROH, in which R^+ is a moderately stable carbonium ion, decompose smoothly slightly above room temperature to yield monoalkyl sulfamyl chlorides, $RNHSO_2Cl$.[6] The reaction is simply effected in practice by dissolving the alcohol (ROH) in hexane,[7] adding equimolar chlorosulfonyl isocyanate ($ClSO_2NCO$), and warming until gas evolution subsides. Taken with the removal of the chlorosulfonyl group the sequence offers a facile synthetic conversion of alcohol to amines.

The scope of the reaction is explored in Table I,[8] along with the order of reactivity of the substrates chosen. The several alcohol derivatives which did not undergo the reaction yielded carbonyl-containing sulfamic polymers when heated to higher temperatures. The stereochemistry of the reaction was investigated with (*S*)(−)-α-phenethyl alcohol and with the 4-*tert*-butyl-1-methylcyclohexanols (cis and trans). In the former case the optical rotation of the product was essentially zero.[9] In the latter case both of the tertiary alcohols yielded an approximately 1:1 mixture of the sulfamyl chloride diastereomers (C-1 epimers). Decomposition of the two related allylic chlorosulfonylurethanes from crotyl and 1-methylallyl alcohols yielded in each case essentially the same ratio of the crotyl and 1-methylallyl products (67:33 from crotyl; 68:34 from 1-methylallyl), analyzed by nmr spectra of the sulfanilide derivative mixture (*cf.* Table I).

Table I. Conversion of Alcohols to Amines

ROH	$RNHSO_2Z$,[a] Z =	% yield (mp, °C)	RNH_2 yield[a]
$(C_6H_5)_2CHOH$	NHNHCOO-*t*-Bu	88 (183)	51
$(C_2H_5)_3COH$	NHC_6H_5	12 (154)	
α-Tetralol	NHC_6H_5	44 (175)	
	NHNHCOO-*t*-Bu	28 (166)	13
$C_6H_5CHOHCH_3$	NH-*t*-Bu(*dl*-)	71 (94)	
	NHNHCOO-*t*-Bu	74 (108)	71
1-Methylcyclohexanol	NHNHCOO-*t*-Bu	78 (110)	80
	*cis*-NHNHCOO-*t*-Bu	55[c]	48
	cis-NHC_6H_5	42[c]	
	trans-NHC_6H_5	43[c]	
$(CH_3)_3COH$	*R*(+)-$NHCH(CH_3)$-C_6H_5	85 (96)	
$CH_2{=}CHCH(CH_3)OH$	NHC_6H_5	42[c]	
$CH_3CH{=}CHCH_2OH$	NHC_6H_5	12[c]	
Cyclohexanol	*b*		
Benzyl alcohol	*b*		
1-Adamantanol	*b*		

[a] Yield from isolated $RNHSO_2NHNHCOO$-*t*-Bu. [b] No decarboxylation of initial chlorosulfonylurethane. [c] Mixture of isomers, see text.

The restriction of substrates ROH to those of moderately good carbonium ions, R^+, and the qualitative order of rates (Table I) parallel the chlorocarbonate decomposition[2] and imply a carbonium ion mechanism.

(1) These reactions include Z = Cl,[2] SR,[3] OCOR,[4] and OAr[5] previously studied.

(2) K. L. Olivier and W. G. Young, *J. Amer. Chem. Soc.*, **81**, 5811 (1959).

(3) J. L, Kice, R. L, Scriven, E. Koubek, and M. Barnes, *ibid.*, **92**, 5608 (1970).

(4) R. C. L. Chow and D. S. Tarbell, *J. Org. Chem.*, **32**, 2188 (1967).

(5) L. M. McDonough, *Chem. Ind. (London)*, 1501 (1965).

(6) The comparable decarboxylative decomposition of carboxylic acid derivatives from chlorosulfonyl isocyanate has already been established (RCOOH + $ClSO_2NCO$ → $RCOOCONHSO_2Cl$ → $RCONHSO_2Cl$ − CO_2); R. Graf, German patent 931,255 (1956); *Chem. Abstr.*, **50**, 7861*a* (1956).

(7) Other solvents gave higher proportions of elimination products.

(8) Satisfactory ir, nmr, and mass spectra as well as elemental analyses were obtained for these derivatives.

(9) Established on the *tert*-butyl sulfamide derivative; authentic optically pure derivative for comparison was prepared from *t*-BuNH-SO_2Cl and *R*(+)-α-phenethylamine.