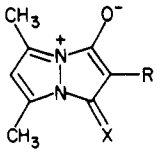
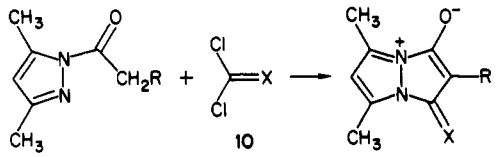
Table I. Some Anhydro-1-hydroxy-5,7-dimethyl-2,3-disubstituted-pyrazolo[1,2-*a*]pyrazolium Hydroxides[9] 11



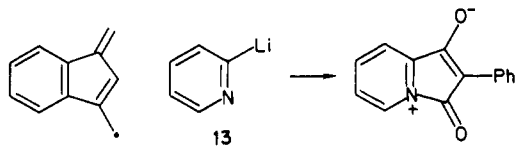
R	X	color/habit	mp °C	ν_{CO}, cm^{-1}	M$^{+\cdot}$ (rel intens)	UV data (CH_3CN) λ_{max}, nm (log ϵ)
Ph	S	lustrous purple plates	155–157	1720	256 (100)	245 (4.16), 287 (4.30), 489 (3.60)
Ph	NTos	orange-red rhombs	196–200 dec	1725	393 (54)	224 (4.44), 263 (4.26), 428 (3.61)
Ph	$C(CN)_2$	purple needles	152–155 dec	1730	288 (100)	252 (4.19), 324 (3.83), 497 (3.83)
CN	O	yellow irregular spears	222–223	1785 1760	189 (100)	224 (4.28), 248 sh (4.25), 360 (2.94)
CN	S	orange needles	241–242	1730	205 (50)	219 (4.06), 225 (4.26), 306 (4.12), 428 (3.71)

of substituents illustrated in Table I. Thus, treatment of 3,5-dimethyl-1-phenylacetylpyrazole[11] (**9**; R = Ph) in benzene with NaH followed by thiophosgene (**10**; X = S) at 0 °C gave anhydro-5,7-dimethyl-1-hydroxy-2-phenyl-3-thioxopyrazolo[1,2-*a*]pyrazolium hydroxide (**11**, R = Ph; X = S) [lustrous purple plates from CCl_4, mp 155–157 °C; λ_{max} CH_3CN nm (log ϵ) 277 (4.36), 469 (3.34); ν_{CO} (KBr) 1720 cm^{-1}; M$^{+\cdot}$ 256 (100%)]. The scope of this approach is illustrated by the variety of substituents[12] shown in Table I.



9 **10** **11**

Other cross-conjugated betaines may also be readily visualized by using the above conceptual approach. Thus, union of a pentadienyl radical **2** with benzene results in the 1,3-dimethyleneindenyl radical **12**, and introduction



12 **13** **14**

of a two-electron nitrogen into **12** leads to three types[13] of cross-conjugated betaines. One of these is represented by **14**, and it has now been prepared by reaction of (chlorocarbonyl)phenylketene (**6**) with 2-pyridyllithium (**13**) at −30 °C in Et_2O. Anhydro-1-hydroxy-3-oxo-2-phenylpyrrolo[1,2-*a*]pyridinium hydroxide (**14**) formed purple plates from acetonitrile, mp 264–268 °C [λ_{max} CH_3CN nm (log ϵ) 221 (4.15), 273 (4.27), 346 (3.93), 515 (3.00); ν_{CO} (KBr) 1735 cm^{-1}; M$^{+\cdot}$ 233 (100%)].

These heterocyclic betaines show a variety of interesting chemical and physical properties. For example, **4** (R = Ph) undergoes facile electrophilic substitution in the benzene ring and cannot be alkylated with Meerwein's reagent. In contrast the corresponding sulfur system reacts at the sulfur atom with triethyloxonium hexafluorophosphate but not with methyl iodide. The spectral data shown in Table I suggests that in the excited state significant intramolecular charge transfer may occur. Details of the scope of these heterocyclic betaines, their synthesis, and physical and chemical characteristics will be described in later publications.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Kevin T. Potts,* William R. Kuehnling
Department of Chemistry
Rensselaer Polytechnic Institute
Troy, New York 12181
Received May 4, 1984

(11) Gilman, H.; Spatz, S. M. *J. Org. Chem.* **1951**, *16*, 1485.
(12) Attempts to make **11** (R = H) are inconclusive, and the preparation of this compound is still being studied. Reaction of 3,5-dimethylpyrazole with malonyl dichloride/Et_3N resulted in electrophilic substitution at the 2-position giving **11** (R = $COCH_2COOEt$).
(13) Variation of the exocyclic substituents as in ref 7 results in 75 possible systems, and variation of the ring atoms increases the total number of possible systems to 225.

A Direct Conversion of Unprotected D-Ribose into Showdomycin and Epishowdomycin

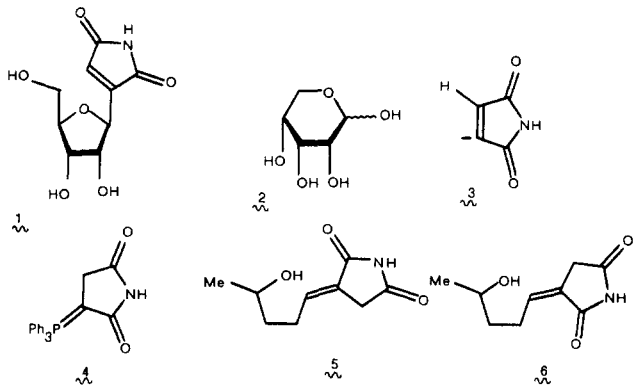
Summary: Reaction of D-ribose with 3-(triphenylphosphorylidene)-1*H*-pyrrole-2,5-dione followed by phenylselenyl chloride–hydrogen peroxide gave showdomycin and epishowdomycin.

Sir: The *C*-nucleoside showdomycin (**1**) is a *Streptomcyes showdoensis* metabolite[1,2] noted both for its antibiotic[3] and antitumoral[4] activities. Several multistage syntheses of this important natural product from both protected carbohydrate[4-6] and noncarbohydrate[7] precursors have been

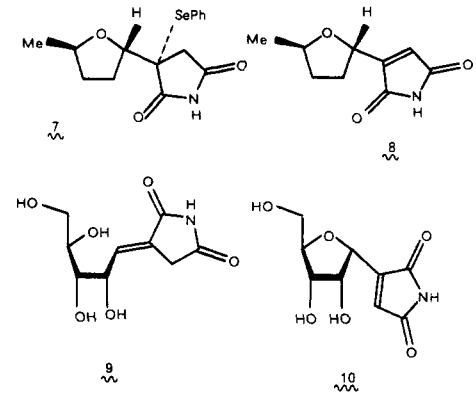
(1) Darnall, K. R.; Townsend, L. B.; Robins, R. K. *Proc. Nat. Acad. Sci. U.S.A.* **1967**, *57*, 548. Nakagawa, Y.; Kano, H.; Tsukuda, Y.; Koyama, H. *Tetrahedron Lett.* **1967**, 4105. Tsukuda, Y.; Nakagawa, Y.; Kano, H.; Sato, T.; Shiro, M.; Koyama, H. *Chem. Commun.* **1967**, 975.
(2) Nishimura, H.; Mayama, M.; Komatsu, Y.; Kato, H.; Shimaoka, N.; Tanaka, Y. *J. Antibiot., Ser. A* **1964**, *17*, 148.
(3) Matsuura, S.; Shiratori, O.; Katagiri, K. *J. Antibiot., Ser. A* **1964**, *17*, 234.
(4) Buchanan, J. G. *Prog. Chem. Org. Nat. Prod.* **1983**, *44*, 243. Inoue, T.; Kuwajima, I. *J. Chem. Soc., Chem. Commun.* **1980**, 251.
(5) Kalvoda, L.; Farkas, J.; Sorm, F. *Tetrahedron Lett.* **1970**, 2297. Buchanan, J. G.; Edgar, A. R.; Power, M. J.; Shanks, C. T. *J. Chem. Soc., Perkin Trans. 1* **1979**, 225. Trummlitz, G.; Moffatt, J. G. *J. Org. Chem.* **1973**, *38*, 1841. Kalvoda, L. *J. Carbohydr., Nucleosides, Nucleotides* **1976**, *3*, 47.
(6) Kane, P. D.; Mann, J. *J. Chem. Soc., Chem. Commun.* **1983**, 224.

0022-3263/84/1949-3673$01.50/0

described. Without exception, in these syntheses, the maleimide ring of 1 was introduced indirectly either via carbacyclic or acyclic β-anomeric substituents on the ribose ring. In addition, only one synthesis to date produced the C-9 skeleton of 1 directly in the first step.[4] We considered that a concise route to 1 should be available via the condensation of D-ribose (2) with a maleimide anion equivalent 3. In addition, we speculated that by suitable choice of 3 it should be possible to directly convert D-ribose (2) into showdomycin (1) *without recourse to classical hydroxyl group protection.*



Ylide 4, readily prepared from maleimide and triphenylphosphine,[8] condensed smoothly with 2-hydroxytetrahydrofuran in acetic acid at room temperature to produce 5 (68–83%) and 6 (0–6%).[9] This reaction clearly refutes the surprising[6,10] claim by Harmon et al. that 4 does not react with lactols.[11] The geometric isomers 5 [^{1}H NMR δ 6.55 (tt, 1 H, J = 7, 2 Hz)] and 6 [^{1}H NMR δ 5.95 (br t, J = 7 Hz)] were readily distinguished by NMR spectroscopy. Reaction of 5 with phenylselenyl chloride in refluxing acetonitrile gave 7 (67%).[12] Subsequent reaction of 7 in dichloromethane with ozone at −78 °C followed by triethylamine at room temperature gave the maleimide derivative 8 (100%). Encouraged by these model studies, we examined the reaction of D-ribose (2) with the ylide 4. In refluxing THF 2 and 4 slowly condensed to produce 9 (74%) [^{1}H NMR δ 6.75 (dt, 1 H, J =



7.5, 2 Hz)] which was obtained as a single geometric isomer. We expected that by analogy with simple seleno-etherification reactions[13] 9 should give rise to the furanose and not the pyranose *C*-glycoside on cyclization. Thus 9 reacted smoothly with phenylselenyl chloride in refluxing *trimethyl borate* to give an unstable product which was not isolated but directly oxidized with excess aqueous hydrogen peroxide (100 vol) in acetonitrile solution. Preparative HPLC on Dupont Zorbax SIL gave showdomycin (1) (13%)[14] and epishowdomycin (10) (41%).[15]

The protocol described here represents a convenient and concise method for the synthesis of showdomycin (1) from D-ribose (2). This chemistry is directly relevant to other *C*-glycosides.

Acknowledgment. We thank the Science and Engineering Research Council and Glaxo Group Research for a C.A.S.E. studentship (H.B.B.) and for the transference of support from Imperial College London to Northwestern University. We also thank Professor J. G. Buchanan of Heriot Watt University, Edinburgh, for authentic samples of natural showdomycin (1) and synthetic epishowdomycin (10), Dr. A. A. L. Gunatilaka for preliminary experiments, and Drs. Stan Roberts and Steven Attwood for helpful discussions.

Supplementary Material Available: X-ray crystal structure analysis of epishowdomycin (10) (7 pages). Ordering information is given on any current masthead page.

(7) Ito, Y.; Arita, M.; Adachi, K.; Shibata, T.; Sawai, H.; Ohno, M. *Nucleic Acids Symp. Ser.* **1981**, *10*, 45. Just, G.; Liak, T. J.; Lim, M.-I.; Potvin, P.; Tsantrizos; Y. S. *Can. J. Chem.* **1980**, *58*, 2024. Sato, T.; Ito, R.; Hayakawa, Y.; Noyori, R. *Tetrahedron Lett.* **1978**, 1829. Kozikowski, A. P.; Ames, A. *J. Am. Chem. Soc.* **1981**, *103*, 3923. Noyori, R.; Sato, T.; Hayakawa, Y. *Ibid.* **1978**, *100*, 2561.

(8) Heyada, E.; Theodoropoulos, S. *Tetrahedron* **1968**, *24*, 2241. Tronchet, J. M. J.; Gentille, B. *Helv. Chim. Acta* **1979**, *62*, 977. Tronchet, J. M. J.; Valero, M. J. *Ibid.* **1979**, *62*, 2788.

(9) New compounds were fully authenticated by spectral and microanalytical data.

(10) There are numerous examples of condensation reaction between stabilized ylides and lactols. For examples, see: Ohrui, H.; Jones, G. H.; Moffatt, J. G.; Madox, M. L.; Christensen, A. T.; Byram, S. K. *J. Am. Chem. Soc.* **1975**, *97*, 4602. Clingerman, M. C.; Secrist, J. A., III. *J. Org. Chem.* **1983**, *48*, 3141.

(11) Harmon, R. E.; Wellman, G.; Gupta, S. K. *Carbohydr. Res.* **1970**, *14*, 123; **1969**, *11*, 574.

(12) The stereochemistry of 7 was determined by nuclear Overhauser effects observed between the C-5-β-methyl and the C-4-β- and C-2-β-hydrogens on the tetrahydrofuran ring.

(13) Nicolaou, K. C.; Magolda, R. H.; Sipio, W. J.; Barnette, W. E.; Lysenko, Z.; Jouillie, M. M. *J. Am. Chem. Soc.* **1980**, *102*, 3784.

(14) The sample of 1 was identical (HPLC, mp, $[\alpha]_D$, IR, ^{1}H NMR, ^{13}C NMR, and mass spectrum) with authentic natural material.

(15) Aslani-Shotorbani, G.; Buchanan, J. G.; Edgar, A. R.; Shanks, C. T.; Williams, G. C. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2267. The sample of 10 showed mp 139–140 °C, $[\alpha]_D$ −76° (lit. mp 139–140 °C, $[\alpha]_D$ −77°). In addition, the IR, ^{1}H NMR, ^{13}C NMR, and mass spectra supported this assignment. To unequivocally rule out the possiblity that this major compound was a pyranose derivative, the structural assignment was confirmed by X-ray crystallography. Subsequent to this determination Professor J. G. Buchanan kindly supplied us with an authentic sample of 10.

Anthony G. M. Barrett,* Howard B. Broughton
Department of Chemistry
Northwestern University
Evanston, Illinois 60201
Received June 1, 1984