thylation of 7 with sodium ethyl thiolate⁹ gave the optically active (-)-HHC, 8 ($\alpha_{\rm D}$ -73.9°, c = 0.014).¹⁰ An identical sequence was carried out on (-)-citronellal and (+)-HHC $(\alpha_{\rm D} + 82.9^{\circ}, c = 0.024)$ was obtained.

Several points in this desilylation-cyclization methodology are noteworthy. Firstly, the bis-silylated derivative need not be isolated and the o-quinone methide can be generated slowly. Secondly, the success of the process for generating the o-quinone methide requires the regioselective desilvlation of the phenol silvl ether with concomitant elimination of trimethylsilanoxide. Finally, the asymmetric induction during the intramolecular Diels-Alder reaction is controlled by the preference for a pseudo-chair conformation in the transition state as shown in Figure 1. This latter aspect was previously manifested in Tietze's work.³

Acknowledgment. We thank Professor E. F. Domino of the Medical School, University of Michigan, for a sample of (-)-THC for spectral comparisons.

Joseph P. Marino,* Scott L. Dax

Department of Chemistry The University of Michigan Ann Arbor, Michigan 48109 Received July 16, 1984

New Heterocyclic Betaines

Summary: Several new types of cross-conjugated, heterocyclic betaines have been prepared from (chlorocarbonyl)phenylketene and, e.g., 1-methylimidazole and pyridine; in an alternative synthetic approach, reaction of 1-(substituted-acetyl)-3,5-dimethylpyrazole with NaH and the electrophilic reagents phosgene, thiophosgene, and other activated geminal dichlorides allowed variation of the exocyclic substituents in new examples of the pyrazolo[1,2-a]pyrazole system.

Sir: In several recent publications,^{1,2} attention has focused on new classes of heterocyclic betaines. The interesting, deep red anhydro-1-hydroxy-3-oxo-2-phenylpyrazolo[1,2a pyrazolium hydroxide¹ (4; R = Ph) and related derivatives are cross-conjugated systems which may be formally derived from the diradical 3 considered to be formed by union of a cyclopentadienyl radical 1 and a pentadienyl radical 2. Replacement of two carbon atoms with two



(1) Potts, K. T.; Kanemasa, S.; Zvilichovsky, G. J. Am. Chem. Soc. 1980, 102, 3971.

two-electron nitrogen atoms in the diradical 3 leads to the betaine 4, which is isoelectronic with the 1,3-dimethylenepentalenyl dianion.³ In this manner one can derive six general types of cross-conjugated betaines containing a [5,5] ring-fused system.⁷ In this paper we describe additional representatives of these cross-conjugated betaines as well as a new route to 4 which enables variation of the exocyclic heteroatoms.

Reaction of 1-methylimidazole (5) with (chlorocarbonyl)phenylketene⁸ (6) in THF at room temperature in the presence of Et₃N gave anhydro-1-hydroxy-7methyl-3-oxo-2-phenylpyrrolo[1,2-a]imidazolium hydroxide⁹ (8) [red spears from EtAc, mp 188–190 °C dec; ν_{CO} (KBr) 1730 cm⁻¹; M⁺ 226 (100%)]. Reaction occurred via the N-3 acylated derivative 7 as this colorless product, on treatment with Et₃N, readily formed 8. Ring closure of



7 in the alternative sense to form the isomeric pyrrolo-[1,2-c]imidazole system was excluded by failure of 1,2dimethylimidazole to form an analogous product. The intermediacy of 7 is consistent with the mechanism proposed for the acid-catalyzed D_2O exchange of H-2 in imidazoles.10

Our earlier synthesis¹ of 4 from (chlorocarbonyl)phenylketene (6) and pyrazole in the presence of Et_3N excluded exocyclic substituents other than oxygen and nonaromatic substituents at position 2 due to difficulties in preparing the appropriate highly reactive species analogous to 6. An alternative synthesis, involving ring closure of substituted 1-acetylpyrazoles with suitable 1,1bielectrophiles in the presence of base now provides ready access to additional representatives of 4 with the variety

(7) In our evaluations, systems differing by replacement of one or more carbon atoms by one-electron nitrogen atoms are considered representatives of the same type. Consequently, variation of the exocyclic oxygen atoms between S, Se, NR, and CR2 in the six systems containing nitrogen results in 90 possible systems. When two-electron heteroatoms other than nitrogen (O, S, and Se) are included in the ring-fused skeleton, the total number of possible betaines is increased to 1035.

(8) Nakanishi, S.; Butler, K. Org. Prep. Proced. Int. 1975, 7, 155. (9) All compounds reported gave satisfactory analytical results ($\pm 0.4\%$ C, H, N) and compatible ¹H NMR spectra.

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⁽⁹⁾ Feutrill, G. I.; Mirrington, R. N. (Tetrahedron Lett. 1970, 16, 1327. (10) IR (CHCl₃): 3580 (s), 3050-2850 (s), 1638 (m), 1580 (m), 1450 (w), 1355 (w), 1140 (w) cm⁻¹; NMR (CDCl₃, 360 MHz): δ 0.88 (t, 3 H), 0.90 (d, 3 H), 1.06 (s, 3 H), 1.25–1.65 (m, 11 H), 1.36 (s, 3 H), 1.85 (m, 2 H), 2.35-2.52 (t and m, 3 H), 3.04 (dm, J = 12.9 Hz, 1 H), 4.68 (s, 1 H), 6.08(d, 1 H) and 6.24 (d, 1 H). Based upon the optical purities of the starting citronellal and citronellol,⁵ the optical rotations of both (-)-HHC and (+)-HHC are within experimental error of the values reported by Tietze et al.3

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⁽³⁾ Heterosubstitution of a m-quinodimethane diradical formed from a propenyl radical and a pentadienyl radical results in cross-conjugated six-membered ring betaines containing pyrimidine,⁴ thiazine,⁵ and triazine⁶ rings.

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 R	x	color/habit	mp °C	$\nu_{\rm CO},~{\rm cm}^{-1}$	M ⁺ · (rel intens)	$\frac{\text{UV data (CH_3CN)}}{\lambda_{\max}, \text{ nm (log } \epsilon)}$
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	0	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-phenylacetylpyrazole¹¹ (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-3thioxopyrazolo[1,2-a]pyrazolium hydroxide (11, R = Ph; X = S) [lustrous purple plates from CCl_4 , mp 155–157 °C; λ_{max} CH₃CN nm (log ϵ) 277 (4.36), 469 (3.34); ν_{CO} (KBr) 1720 cm⁻¹; M⁺ 256 (100%)]. The scope of this approach is illustrated by the variety of substituents¹² shown in Table I.



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



of a two-electron nitrogen into 12 leads to three types¹³ 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 Et₂O. Anhydro-1-hydroxy-3-oxo-2-phenylpyrrolo[1,2-a]pyridinium hydroxide (14) formed purple plates from acetonitrile, mp 264–268 °C [λ_{max} CH₃CN nm $(\log \epsilon)$ 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

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

Summary: Reaction of D-ribose with 3-(triphenylphosphorylidene)-1H-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 antibiotic³ and antitumoral⁴ activities. Several multistage syntheses of this important natural product from both protected carbohydrate⁴⁻⁶ and noncarbohydrate⁷ precursors have been

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⁽¹²⁾ Attempts to make 11 (R = H) are inconclusive, and the prepa-(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/Et₃N resulted in electrophilic substitution at the 2-position giving 11 ($R = COCH_2COOEt$).

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