of tetra-*n*-butyl ammonium bromide in 40 mL of water was added a solution of 15.5 g (0.10 mol) of *p*-methylbenzoyl chloride in 150 mL of methylene chloride all at once. In about 10 min the reaction temperature had risen to 32 °C. After 50 min, infrared analysis revealed the presence of cyanohydrin ester (1730 cm^{-1}) and acyl cyanide (1680 cm^{-1}). An additional quantity of 0.10 g (0.0026 mol) of sodium borohydride in 5 mL of water was added. After an additional 70 min the organic layer was removed, dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo at 30 °C. Crude yield was 12.2 g (92.2%) of cyanohydrin ester **2c** as an orange liquid, identical in all respects with a sample of **2c** prepared from *p*-tolualdehyde cyanohydrin, *p*-methylbenzoyl chloride, and triethylamine.

(B) Cyanohydrin Acetates from Acyl Cyanides. *m*-Tolualdehyde Cyanohydrin Acetate (7). A magnetically stirred solution of 3.0 g (0.0206 mol) of *m*-methylbenzoyl cyanide[14] in 37 mL of acetic anhydride was treated with 0.60 g (0.0158 mol) of finely ground sodium borohydride in 0.10-g portions over a 1-h period. Thirty minutes after the final addition volatiles were removed under reduced pressure. The residue was treated with water and methylene chloride. The organic layer was stirred with 5% aqueous sodium hydroxide to remove unreacted acyl cyanide, washed with water, dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo at 30 °C. Crude yield was 2.6 g (66.5%) of **7**, IR ν_{max} (neat) 1755 cm^{-1}, identical in all respects with a sample prepared from *m*-tolualdehyde cyanohydrin, acetyl chloride, and triethylamine.

Acknowledgment. I am grateful to Dr. Ashe Freiberg and Mr. Peter Letchworth for performing the insecticidal activity measurements.

Registry No. **1a**, 613-90-1; **1b**, 5955-74-8; **1c**, 14271-73-9; **2a**, 4242-46-0; **2b**, 75599-78-9; **2c**, 75599-79-0; **7**, 75599-80-3; benzoyl chloride, 98-88-4; *m*-methylbenzoyl chloride, 1711-06-4; *p*-methylbenzoyl chloride, 874-60-2; benzaldehyde cyanohydrin acetate, 5762-35-6; *p*-tolualdehyde cyanohydrin acetate, 75599-81-4.

Synthesis of 4,4′-(Ethanediylidene)bis(4*H*-pyran) and -(thiopyran) Derivatives

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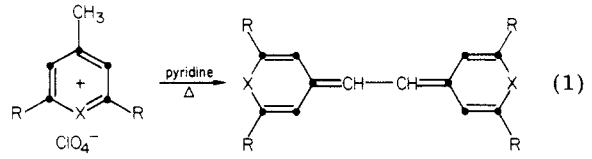
The 2,2′,6,6′-tetraaryl-$\Delta^{4,4'}$-bis(4*H*-pyrans) and their sulfur analogues are of interest as electron-donating materials that form conducting charge-transfer salts with suitable acceptors such as tetracyanoquinodimethane.[1,2] We have investigated the related ethanediylidene bispyran derivatives **1** and found that they also form conducting salts. We had shown previously that **1** can be prepared by heating a pyridine solution of certain pyrylium and thiopyrylium salts as illustrated in eq 1.[3] This method



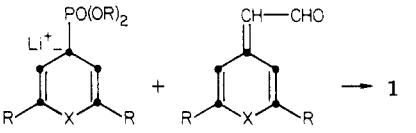
(1)

1

X = O, S

is not general, since **1** (X = O; R = phenyl) could not be prepared, and the method cannot be used to prepare *unsymmetrical* derivatives with differently substituted pyran or thiopyran rings. We now describe a general method for synthesizing a variety of symmetrical and unsymmetrical 4,4′-(ethanediylidene)bis(4*H*-pyrans) and -(thiopyrans).

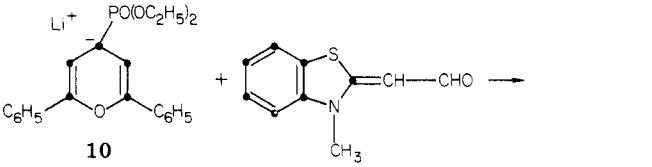
The general method is based on the reaction of a phosphonate anion **2** with aldehydes **3** to yield **1**. Since a variety of anions **2** are available,[4,5] and the aldehydes are readily prepared from methyl-substituted pyrylium salts,[6] the method can be used to prepare many bispyrans.



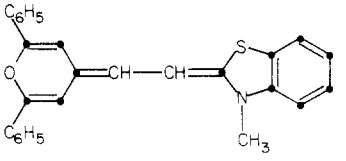
2 **3**

Table I lists the derivatives of **1** that were prepared by this procedure.

The method also was used to prepare **12**, which has different heterocyclic rings.

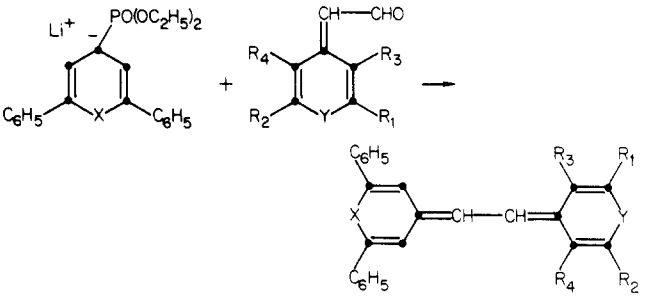


10 **11**



12

Table I. Bispyran Derivatives[a]



compd	R	X	Y	mp, °C	% yield
4	$R_1 = R_2 = C_6H_5$; $R_3 = R_4 = H$	O	O	297-298	76
5	$R_1 = R_2 = C_6H_5$; $R_3 = R_4 = H$	S	S	301-302	29
6	$R_1 = R_2 = C_6H_5$; $R_3 = R_4 = H$	O	S	257-258	6.2
6	$R_1 = R_2 = C_6H_5$; $R_3 = R_4 = H$	S	O	257-258	3.7
7	R_1R_3 = benzo; R_2R_4 = benzo	O	S	304-305	62
8	R_1R_3 = 1,2-naphtho; R_2R_4 = 1,2-naphtho	O	O	273-274	40
9	$R_1 = C_6H_5$; $R_3 = H$; R_2R_4 = benzo	O	S	184-185	61

[a] Satisfactory analytical data were reported for all compounds in this table.

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Experimental Section

Melting points were determined with a Mel-Temp apparatus and are uncorrected. It was difficult to obtain NMR spectra of the bispyrans because of their low solubility. The mass spectra were determined for all compounds and show a characteristic large peak for M^+ (relative intensity 100%) and M^{2+} (relative intensity 20–40%), but all other peaks are less than 1%. The mass spectra were obtained on an AEI MS-30 mass spectrometer, absorption spectra on a Cary-17 spectrometer, and IR spectra on a Beckman IR 4200 spectrometer.

4,4′-(1,2-Ethanediylidene)-2,2′,6,6′-tetraphenylbis(4*H*-pyran) (4). A suspension of 1.95 g (5.9 mmol) of 2,6-diphenylpyrylium perchlorate in 50 mL of dry tetrahydrofuran was stirred under argon and cooled in a dry ice–acetone bath. A 1.1 M solution (5.4 mL, 5.9 mmol) of sodium diethylphosphonate[7] was added by syringe, and the stirring was continued until a clear solution was obtained (about 10 min). To this solution was added 2.4 mL (5.9 mmol) of 2.5 M butyllithium and after 5 min 1.63 g (5.9 mmol) of 2,6-diphenyl-4-(formylmethylene)-4*H*-pyran. The reaction mixture was stirred for 1 h at −78 °C, allowed to stand overnight at room temperature, and then evaporated to dryness. The residue was dissolved in methylene chloride and passed through a column of Florisil (eluted with methylene chloride). The eluant was evaporated to dryness, and the residue was recrystallized twice from toluene: IR (KBr) 1659, 1625, 1601, 1581, 1495, 1451, 1345, 1288, 1244 cm^{-1}; mass spectrum, *m/e* 490, 385, 245, 105, 77; absorption spectrum (CH_2Cl_2) 478 (6.43×10^4), 280 (2.4×10^4), 256 nm (2.5×10^4).

The other ethanediylidene dimers in Table I were prepared in the same manner from the appropriate starting materials. The spectral properties of these compounds are collected in Table II (see supplementary material).

Compound **12** was prepared by the method described for **4** from 2,6-diphenylpyrylium perchlorate (12 mmol) and 2-(formylmethylene)-1-methylbenzothiazolene (12 mmol), giving 0.83 g (17%) of **12**, mp 227–228 °C.

Anal. Calcd for $C_{27}H_{21}NOS$: C, 79.6; H, 5.2; N, 3.4. Found: C, 79.3; H, 5.0; N, 3.3.

Registry No. 2 (X = O), 75548-91-3; **2** (X = S), 75548-92-4; **3** ($R_1 = R_2 = Ph$; $R_3 = R_4 = H$; Y = O), 20399-89-7; **3** ($R_1 = R_2 = Ph$; $R_3 = R_4 = H$; Y = S), 75548-93-5; **3** (R_1R_3 = benzo; R_2R_4 = benzo; Y = S), 56389-52-7; **3** (R_1R_3 = 1,2-naptho; R_2R_4 = 1,2-naptho; Y = O), 75548-94-6; **3** ($R_1 = Ph$; $R_3 = H$; R_2R_4 = benzo; Y = S), 20399-91-1; **4** ($R_1 = R_2 = Ph$; $R_3 = R_4 = H$; X = O; Y = O), 62041-62-7; **5** ($R_1 = R_2 = Ph$; $R_3 = R_4 = H$; X = S; Y = S), 51829-03-9; **6** ($R_1 = R_2 = Ph$; $R_3 = R_4 = H$; X = O; Y= S), 75548-95-7; **7** (R_1R_3 = benzo; R_2R_4 = benzo; X = O; Y = S), 75548-96-8; **8** (R_1R_3 = 1,2-naptho; R_2R_4 = 1,2-naptho; X = O; Y = O), 75548-97-9; **9** ($R_1 = Ph$; $R_3 = H$; R_2R_4 = benzo; X = O, Y = S), 75548-98-0; **11**, 4616-17-5; **12**, 75558-43-9.

Supplementary Material Available: Spectral data for compounds **5**–**9** and **12** (2 pages). Ordering information is given on any current masthead page.

(7) Commercially available from Organometallics, Inc., East Hampstead, NH.

Optically Active Amines. 29.[1] Application of the Salicylidenimino Chirality Rule to Amino Sugars

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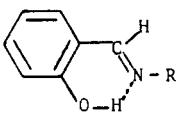
Some time ago, Inouye[3–5] prepared the *N*-salicylidene derivatives of some amino sugars and reported the optical rotatory dispersion (ORD) and circular dichroism (CD) spectra of these derivatives. He suggested the use of such spectra for the determination of the configuration of the amino group in monosaccharides[3,4] and as a means of identification of amino oligosaccharide antibiotics.[5]

In methanol, the *N*-salicylidene derivatives of monosaccharides generally show Cotton effects (CEs) of the same sign near 405, 315, and 255 nm. The latter two are assigned to $\pi \rightarrow \pi^*$ electronic transitions of the hydrogen-bonded salicylidenimino (SI) group (**1**) and that near



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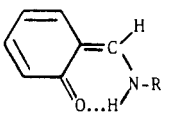

2

405 nm to a transition of the quinoid tautomer **2**.[6,7] In dioxane, the proportion of the quinoid tautomer is reduced in the less polar solvent,[7] and the 405-nm CE is weak and is usually not observed while those near 315 and 255 nm have enhanced intensities.

Inouye concluded that for D-glucose derivatives, positive CEs are correlated with the D (*S*) configuration of the 2-SI group and negative CEs with the L (*R*) configuration of the 1- and 3-SI groups.[3] Extension of the correlation to mannose derivatives was less successful.[3]

We now note, however, that the salicylidenimino chirality rule[8] can be used to correlate the sign of the observed CEs near 315 and 255 nm with the absolute configuration of many amino monosaccharides (Table I), much the same as can be done for similar derivatives of terpene[9] and steroidal amines.[10] The rule is based on the model that the 315- and 255-nm CEs originate from interaction of the respective transition moments of the hydrogen-bonded SI chromophore with bond transition moments in the rest of the molecule. The sign of a contribution to the CEs by a given bond usually can be determined from the chirality that the bond has with the attachment bond of the SI group, a positive contribution for positive chirality (right-handed screw) and negative for negative chirality (left-handed screw).[8] In cases where these two bonds are coplanar, the chirality that the bond has with transition moments of the SI chromophore, the moments situated at the center of the benzene ring with long axis polarization, is used. The contribution of a C–H bond is neglected, and that of a C–C bond outweighs that of a C–O bond.[11,12] When a C–C or C–O bond is vicinal to the SI attachment bond, its contribution predominates unless cancellation occurs. The preferred chair conformation of the tetrahydropyran ring of a hexose makes the ring bond contributions for an equatorial or axial 3-SI group negligible due to complete mutual cancellation as a result of symmetry.

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