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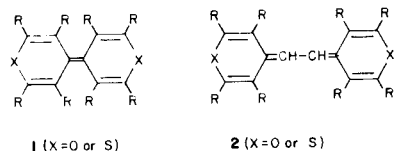
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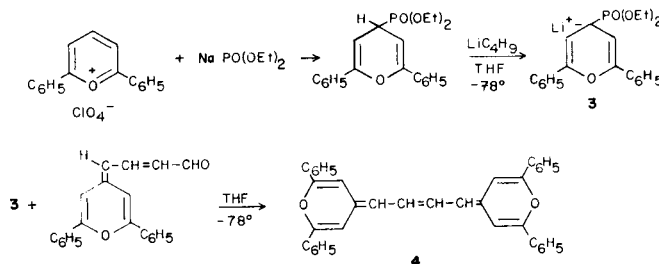
4,4'-(But-2-ene-1,4-dienylidene)-bi-4*H*-pyran and thiopyran derivatives were prepared by allowing the anion prepared from diethyl 4-(2,6-diphenyl-4*H*-pyranyl)phosphonate to react with 4-pyranylidene butenaldehydes or the corresponding thiopyranaldehydes. The oxidation potentials are compared of some bi-4*H*-pyrans and thiopyrans with zero, two, and four methenyl groups separating the heterocyclic nuclei.

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We have investigated new methods for synthesizing $\Delta^{4,4'}$ -bi-4*H*-pyrans and thiopyrans (**1**, X = O or S) (**1-4**), compounds which can form conducting charge-transfer salts (**5**). For studying the effect of changes in the structure of **1** on their physical properties, we prepared derivatives of **1** with an ethanedilydene group separating the heterocyclic nuclei (**2**) (**6**).



The synthetic procedure used to prepare **2** (**6**) was extended to include tetramethenyl derivatives and is illustrated by the preparation of **4**. This method seems to be general and can be used to synthesize symmetrical and unsymmetrical homologs. The unsaturated aldehydes used in



this synthesis were prepared by the condensation of diethylaminoacrolein with 4-methylpyrylium and thiopyrylium salts and their benzo[*b*]homologs (**7**). Table I lists the tetramethenyl bipyrans and thiopyrans that were prepared. The yield of **4** was much higher than that of the other derivatives because the insolubility of **4** greatly decreased losses during work-up.

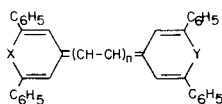
Compounds can undergo two reversible one-electron oxidations. Hünig *et al.* (**8**) reported the cyclic voltam-

Table I

Tetramethylene Bipyran and Thiopyran Derivatives

Compound Number	R	X	Y	M.p. °C	Yield %	Anal. C	Calcd. H	(Found) N	Absorption Spectra in Dichloromethane λ -max ($\epsilon \times 10^{-3}$)	
4	R ₁ = R ₂ = R ₅ = R ₆ = phenyl R ₃ = R ₄ = R ₇ = R ₈ = H	O	O	288-289	93	88.2	5.4		512 (68.0)	275 (25.0)
									489 (70.0)	246 (28.0)
5	R ₁ = R ₂ = R ₅ = R ₆ = phenyl R ₃ = R ₄ = R ₇ = R ₈ = H	S	O	251-252	15	85.7	5.3	6.0	510 (72.0)	
									280 (20.4)	238 (29.6)
6	R ₁ = R ₂ = R ₅ = R ₆ = phenyl R ₃ = R ₄ = R ₇ = R ₈ = H	S	S	276-277	24	83.3	5.1	11.7	533 (81.7)	285 (40.7)
									505 (73.5)	237 (34.0)
7	R ₁ = R ₃ = benzo, R ₂ = phenyl R ₄ = R ₇ = R ₈ = H	S	O	237-238	20	85.4	5.1	6.3	503 (67.0)	
									252 (32.0)	

Table II
Oxidation Potentials of $\Delta^{4,4'}$ -Bi-4*H*-pyrans and Thiopyrans (a)



X	Y	n	Wave I		Wave II		Δ (b)
			Forward	Reverse	Forward	Reverse	
O	O	0	+0.17	+0.11	+0.49	+0.43	0.32
			+0.17	+0.13	+0.50	+0.45	
S	S	0	+0.31	+0.24	+0.52	+0.45	0.21
			+0.33	+0.24	+0.55	+0.45	
O	S	0	+0.26	+0.19	+0.57	+0.42 (adsorption)	0.27
			+0.27	+0.17	+0.59	+0.32 (adsorption)	
O	O	1	+0.13	+0.06	+0.47	+0.41	0.34
			+0.14	+0.05	+0.48	+0.40	
S	S	1	+0.22	+0.16	+0.47	+0.42	0.24
			+0.42	+0.13	+0.51	+0.40	
O	S	1	+0.15	+0.09	+0.46	+0.40	0.31
			+0.17	+0.07	+0.49	+0.39	
O	O	2	+0.22	+0.16	+0.42	+0.36	0.20
			+0.23	+0.14	+0.44	+0.35	
S	S	2	+0.24	+0.18	+0.37	+0.31	0.13
			+0.25	+0.17	+0.39	+0.30	
O	S	2	+0.20	+0.14	+0.35	+0.30	0.16
			+0.21	+0.13	+0.38	+0.29	

(a) The oxidation potentials were determined at a concentration of $5 \times 10^{-4}M$ in methylene chloride; 0.1*M* tetrabutylammonium fluoroborate; the first value is for a platinum and the second for a glassy carbon electrode; SCE saturated aqueous chloride; 0.1 V/second. (b) The difference in the average value for the forward and reverse potentials of Waves I and II, using the potentials obtained with a platinum electrode.

metry of the 2,2',6,6'-tetraphenyl derivatives of **1** (X = O,O and S,S). We thought that separating the heterocyclic rings by an increasing number of methenyl groups would decrease the difference between the first and second oxidation potentials. Table II gives the oxidation potentials for a series of bipyrans and bithiopyrans with zero, two, and four methenyl groups separating the heterocyclic nuclei. Unexpectedly, the dimethenyl compounds (**2**) actually showed an increase in the difference between the potentials compared to **1**, but for the tetramethenyl series, the difference in potentials was considerably smaller than for the corresponding derivatives of **1**. The dithia derivatives were more readily oxidized than the corresponding dioxo compounds, and the unsymmetrical homologs showed an oxidation potential that was approximately the mean of the values for the symmetrical compounds.

EXPERIMENTAL

Melting points were obtained on a Mel-Temp apparatus and are uncorrected. Cyclic voltammograms were obtained by using a Heath polarography system model EUQ-401. We could not obtain the nmr spectra of these compounds because of their poor solubility. The mass spectra were determined for all the compounds, and large signals were obtained for M^+ and M^{2+} , a general characteristic for all of the bi-4*H*-pyran

and thiopyran derivatives that we prepared (4).

The preparation of **4** is given in detail. The other compounds were prepared similarly from **1** and the corresponding aldehyde; for compound **5**, the sulfur analog of **1** was used.

4,4'-(But-2-ene-1,4-dienylidene)-2,2',6,6'-tetraphenyl-bi-4*H*-pyran (**3**).

A suspension of 0.98 g. (3 mmoles) of 2,6-diphenylpyrylium perchlorate in 35 ml. of dry tetrahydrofuran under argon was stirred and cooled in a dry ice bath and acetone bath, and 2.8 ml. (3 mmoles) of 1.1*M* sodium diethylphosphonate (**9**) in benzene was added by syringe. The mixture was stirred until a clear solution was obtained, and 1.2 ml. (3 mmoles) of 2.5*M* *n*-butyllithium was added and the blue solution was stirred for 5 minutes. To the solution was added 0.9 g. (3 mmoles) of 2,6-diphenyl-4-(3-formylprop-2-enylidene)-4*H*-pyran, and the reaction mixture was stirred for 1 hour in the cooling bath and then allowed to stand overnight at room temperature. The red solid was collected and recrystallized from toluene, giving 1.45 g. of **3**. The mass spectrum shows peaks at m/e 516 (M^+), 411, 258 (M^{2+}), 105 and 77.

The compounds listed in Table I were prepared from the appropriate starting materials by the method described for **3**. However, these compounds were more soluble than **3**, and a different method was used for product isolation. The reaction mixture, after standing overnight, was evaporated to dryness and chromatographed on silica gel (activity 3) eluting with methylene chloride and petroleum ether (1:1 volume). The colored first zone was collected, the solvent was removed, and the residue was recrystallized from toluene.

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ing the redox potentials using cyclic voltammetry.

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