This compound is identical with an authentic sample prepared from diethyl (2,6-diphenyl-4*H*-thiopyran-4-yl)phosphonate (**7**).

Synthesis of $\Delta^{4,9'}$-2,6-Diphenyl-4-(9'-thioxanthenyl]-4*H*-thiopyran (10) from Dimethyl (2,6-Diphenyl-2*H*-thiopyran-4-yl)phosphonate (25). To a solution of 450 mg (1.26 mmol) of **25** in 50 mL of dry THF at -78 °C under argon was added dropwise 1.2 equiv of LDA prepared at room temperature from 155 mg of diisopropylamine and 0.63 mL of *n*-BuLi (2.4 M in hexanes). A solution of 260 mg of thioxanthen-9-one (**9**) in 20 mL of dry THF was added immediately to this dark blue Wittig–Horner reagent, and the reaction mixture was kept at -78 °C for at least 1 h before being allowed to warm slowly to room temperature. After being stirred at ambient temperature overnight under argon, the reddish brown solution was worked up in the usual manner to give 600 mg of a reddish brown gum. This was purified by boiling with 120 mL of heptane, and the desired product, which is insoluble in hot heptane, was collected by filtration to give 80 mg (14%) of **10**.

This material is identical with an authentic sample prepared independently from diethyl (2,6-diphenyl-4*H*-thiopyran-4-yl)phosphonate (**7**).

Acknowledgment. We thank Mr. Walter G. Dunn of the Kodak Industrial Laboratory for obtaining the high-resolution mass spectra.

Registry No. **6**, 13586-29-3; **7**, 73453-36-8; **9**, 492-22-8; **9a**, 100-10-7; **10**, 73453-37-9; **10a**, 73453-38-0; **11**, 73453-39-1; **17** (R = c-C$_6$H$_{11}$), 68883-88-5; **20**, 37014-01-0; **21**, 62310-05-8; **22**, 62310-06-9; **23**, 73453-40-4; **25**, 73453-41-5; sodium diethyl phosphonate, 2303-76-6; diethyl hydrogen phosphite, 762-04-9.

Synthesis of Unsymmetrical $\Delta^{4,4'}$-Bi-4*H*-pyrans and -thiopyrans[1]

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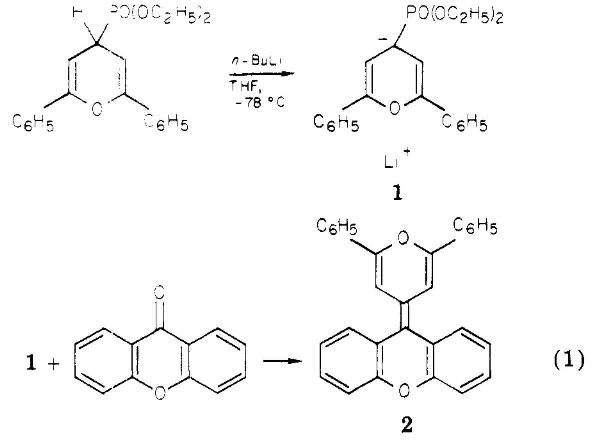
Unsymmetrical $\Delta^{4,4'}$-bi-4*H*-pyrans and -thiopyrans are prepared from the Wittig reagent which is derived from (4*H*-pyran-4-yl)triphenylphosphonium salts or the thio analogues by allowing the reagent to react with a pyrylium or thiopyrylium salt with an unsubstituted 4-position.

We recently described the preparation of $\Delta^{4,4'}$-bi-4*H*-pyrans and thiopyrans which were unsymmetrically substituted about the exocyclic double bond by the reaction of the anion of a (4*H*-pyran-4-yl)phosphonate or the thio analogue with certain carbonyl compounds.[2,3] A typical example is given in eq 1. This reaction is limited in scope to certain reactive carbonyl compounds. For example, 2,6-diphenyl-4*H*-thiopyran-4-one does not react with 1. Deactivated aldehydes, however, react with 1; e.g., 4-(dimethylamino)benzaldehyde and 1 gave 4-[[4-(dimethylamino)phenyl]methylene]-2,6-diphenyl-4*H*-pyran (**3**) in 50% yield.

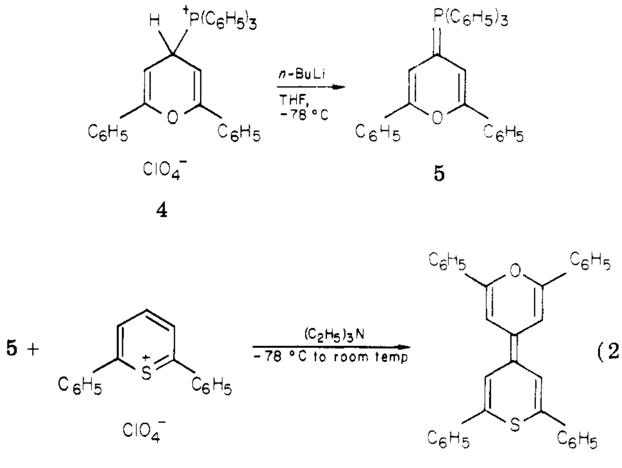


1

2

(1)

We now report a more general method for the preparation of unsymmetrically substituted bipyrans by use of triphenylphosphoranes as outlined in eq 2 for the preparation of **6**. Other examples that were prepared by this method with various phosphonium salts and pyrylium or thiopyrylium salts are collected in Table I. The phosphonate anion **1** did not react with 2,6-diphenylpyrylium or -thiopyrylium perchlorate to give bipyran derivatives.



4

5

6

(2)

The yields of bipyrans prepared by the method shown in eq 2 are 30–40%. These low yields are due in part to the insolubility of the phosphonium salt and the pyrylium salt in tetrahydrofuran. We have unsuccessfully investi-

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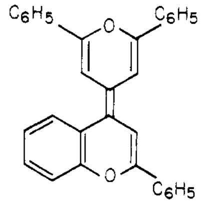
[1] Presented in part at the Wurster Centennial Symposium at the 178th National Meeting of the American Chemical Society, Washington, DC, Sept 10–14, 1979.

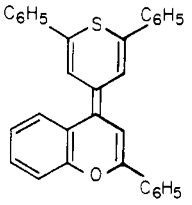
[2] Chen, C. H.; Reynolds, G. A. *J. Org. Chem.*, preceding two papers in this issue.

[3] In the course of this work the synthesis of unsymmetrical tetrathiofulvalenes by a similar procedure was published. Connella, N. C.; Cava, M. P. *J. Org. Chem.* **1978**, *43*, 369.

Table I. $\Delta^{4,4'}$-Bi-4*H*-pyran Derivatives



7

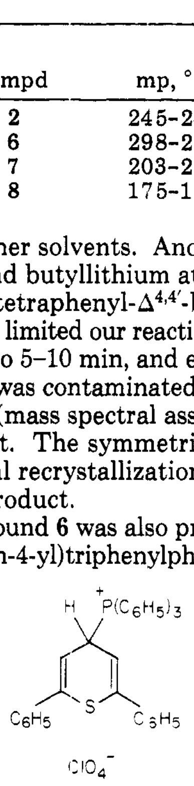


8

compd	mp, °C	yield, %	empirical formula	anal. calcd/found C	H	S
2	245-246	42	$C_{30}H_{20}O_2$	87.4/87.1	4.9/4.6	
6	298-299	30	$C_{34}H_{24}OS$	85.0/85.1	5.0/4.9	6.7/6.5
7	203-204	36	$C_{32}H_{22}O_2$	87.6/87.3	5.1/5.3	
8	175-176	32	$C_{32}H_{22}OS$	84.5/84.1	4.9/4.7	7.1/6.8

gated other solvents. Another factor to be considered is that 4 and butyllithium at −78 °C in THF (45 min) gave 2,2′,6,6′-tetraphenyl-$\Delta^{4,4'}$-bi-4*H*-pyran in 70% yield. We therefore limited our reaction time for preparing the Wittig reagent to 5–10 min, and even under these conditions the product was contaminated with 2–5% of the symmetrical bipyran (mass spectral assay) derived from the phosphonium salt. The symmetrical bipyrans were removed by fractional recrystallization or chromatography of the reaction product.

Compound 6 was also prepared from (2,6-diphenyl-4*H*-thiopyran-4-yl)triphenylphosphonium perchlorate (**9**)[4] and 2,6-diphenylpyrylium perchlorate in slightly lower yield (20%). The dimer 2 was prepared as described above from (9-xanthenyl)triphenylphosphonium perchlorate (**10**)[4] and 2,6-diphenylpyrylium perchlorate.



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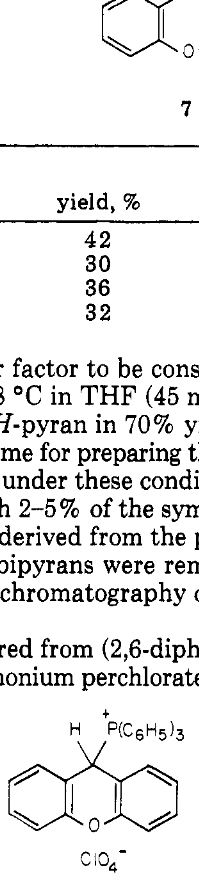

10

Experimental Section

Melting points were obtained on a Mel-Temp apparatus and are uncorrected. The NMR spectrum was obtained on a Varian EM-390 spectrometer.

Phosphonium Salts. A mixture of 10 mmol each of the pyrylium or thiopyrylium salt and triphenylphosphine in 25 mL of acetonitrile was stirred for 2 h. The yellow color was completely discharged, and the white precipitate was collected and washed with acetonitrile. Satisfactory combustion analyses were obtained for each compound. The phosphonium salts were prepared previously by using a slightly different procedure,[4] and the reported melting points are given as follows.

(2,6-Diphenyl-4*H*-pyran-4-yl)triphenylphosphonium perchlorate (**4**) from 2,6-diphenylpyrylium perchlorate: mp 180–181 °C dec (lit.[4] mp 163.5 °C), yield 92%.

(2,6-Diphenyl-4*H*-thiopyran-4-yl)triphenylphosphonium perchlorate (**9**) from 2,6-diphenylthiopyrylium perchlorate: mp 135–136 °C (lit.[4] mp 140–142 °C), yield 94%.

(9-Xanthenyl)triphenylphosphonium perchlorate (**10**) from xanthylium perchlorate: mp 241–242 °C (lit.[4] mp 234–235 °C), yield 94%.

General Procedure for the Preparation of the Mixed Dimers. The procedure will be illustrated by describing the preparation of 6. A suspension of 1.2 g (2 mmol) of 4 in 35 mL of dry tetrahydrofuran was stirred under argon and chilled in a dry ice/acetone bath. A 2.5 M solution of butyllithum (0.9 mL) was added, and after the mixture was stirred for 5 min, 0.7 g (2 mmol) of 2,6-diphenylthiopyrylium perchlorate[5] was added. The mixture was stirred at −78 °C for 1 h, and 5 mL of triethylamine was added. The mixture was allowed to warm to room temperature and allowed to stand overnight. The reaction mixture was poured through a short column of silica gel and eluted with petroleum ether and methylene chloride (2:1). The eluent was evaporated, and the residue was recrystallized from toluene, giving 0.31 g (32%) of black crystals. The solid, which contained about 5% of 7 (by mass spectrum), was recrystallized three times from toluene and once from ethyl acetate: mp 287–288 °C; NMR ($CDCl_3$) δ 6.62 (s, 2 H), 6.88 (s, 2 H), 7.35–7.8 (m, 20 H).

Compound 7 was prepared from 4 and flavylium perchlorate, and 8 was prepared from 9 and flavylium perchlorate.

4-[[4-(Dimethylamino)phenyl]methylene]-2,6-diphenyl-4*H*-pyran (3). A suspension of 2 g (6 mmol) of 2,6-diphenylpyrylium perchlorate in 50 mL of dry THF was stirred under argon at −78 °C, and 5.6 mL (6 mmol) of 1.1 M sodium diethyl phosphonate[6] in benzene was added by syringe. The solid dissolved within 5 min, giving a colorless solution. After the solution was stirred 10 min more, 2.5 mL of 2.5 M butyllithium was added, followed after 5 min by 0.9 g (6 mmol) of *p*-(dimethylamino)benzaldehyde. The solution was stirred for 1 h at −78 °C and allowed to warm to room temperature, and saturated ammonium chloride and ether were added. The ether phase was separated and dried ($MgSO_4$), and the solvent was removed. The residue was recrystallized from acetonitrile, giving 1.28 g of 3, mp 180–181 °C.

Anal. Calcd for $C_{26}H_{23}NO$: C, 85.4; H, 6.2; N, 3.8. Found: C, 85.7; H, 6.3; N, 4.0.

Registry No. 2, 73453-48-2; 3, 73453-49-3; 4, 21186-83-4; 6, 73453-50-6; 7, 73453-51-7; 8, 73453-52-8; 9, 23092-12-8; 10, 22730-67-2; triphenylphosphine, 603-35-0; 2,6-diphenylpyrylium perchlorate, 3558-68-7; 2,6-diphenylthiopyrylium perchlorate, 13586-29-3; xanthylium perchlorate, 2567-19-3; flavylium perchlorate, 6272-41-9; *p*-(dimethylamino)benzaldehyde, 100-10-7.

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[4] Zhdanov, Y. A.; Krivun, S. V.; Polenov, V. A. *Khim. Geterotsikl. Soedin.* **1969**, 368.

[5] Reynolds, G. A.; Chen, C. H.; Van Allan, J. A. *J. Org. Chem.* **1979**, *44*, 4456.

[6] Obtained from Organometallics, Inc., Hampstead, NH.