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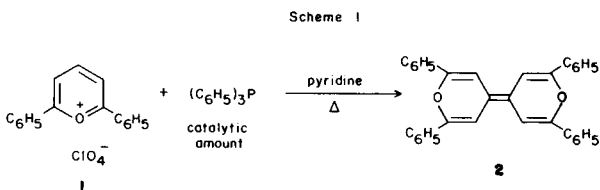
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The phosphonium salt from tributylphosphine and 2,6-di(4-methoxyphenyl)pyrilium perchlorate (**3**) reacted with diisopropylethylamine in acetonitrile to give 2,2',6,6'-tetra(4-methoxyphenyl)- $\Delta^{4,4'}$ -bi-4*H*-pyran in quantitative yield. The reaction of **3** and other 4*H*-pyrilium salts with tertiary amines gave 4*H*-pyrans.

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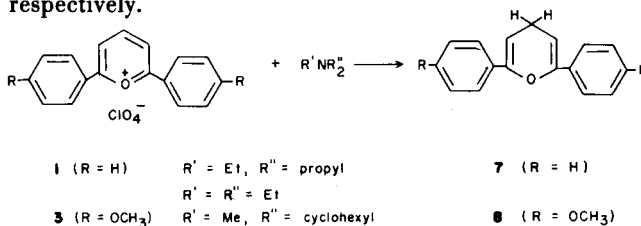
We have described the synthesis of 2,2',6,6'-tetraphenyl- $\Delta^{4,4'}$ -bi-4*H*-pyran (**2**) by the method shown in Scheme I (1). This method was not general; one compound that could



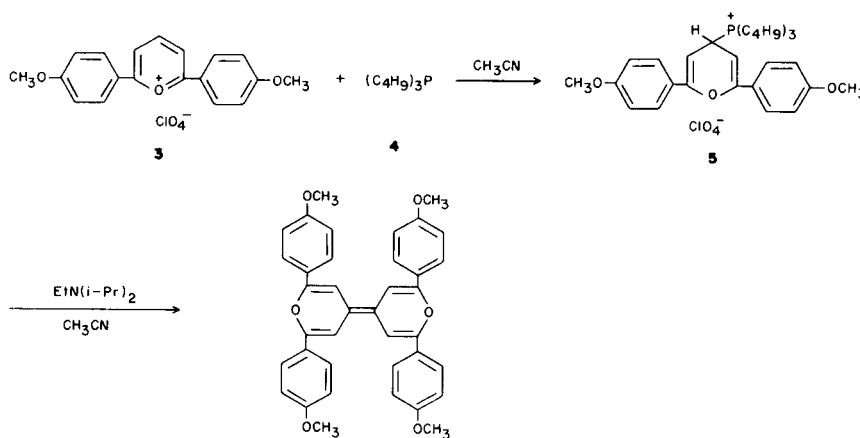
not be prepared was the tetra-*p*-methoxyphenyl derivative **6** (**1**), owing to the inertness of 2,6-di(4-methoxyphenyl)pyrilium perchlorate (**3**) to triphenylphosphine. We report here a method for preparing the methoxy-substituted dimer (**6**) and discuss several other examples that could not be prepared by the method shown in Scheme I.

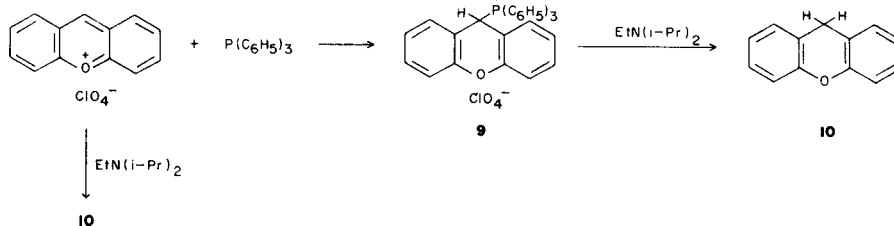
Our strategy for preparing **6** was to use tributylphosphine (**4**) in place of the less reactive triphenylphosphine. The reaction was run first with **1**. A solution of the pyrilium salt **1** and **4** gave a phosphonium salt in 78% yield, but refluxing the phosphonium salt in pyridine for 4 hours gave no reaction. The dimer **2** was obtained in quantitative yield by refluxing the phosphonium salt with diisopropylethylamine in acetonitrile for 2 hours. This procedure was then repeated with **3** and **4**, and the phosphonium salt **5** was obtained in 93% yield and the dimer **6** in 81% yield.

In Scheme I, a catalytic amount of triphenylphosphine is used. When we used a catalytic amount of tributylphosphine with **3**, diisopropylethylamine, and acetonitrile, the dimer **6** was not formed. The isolated product was the reduced pyrilium salt, 2,6-di(4-methoxyphenyl)-4*H*-pyran (**7**). The reaction was repeated with **3**, using only the tertiary amine and acetonitrile, and again **7** was obtained. Compound **7** was prepared by sodium borohydride reduction of the pyrilium salt **3** (by the method used for the preparation of 2,6-diphenyl-4*H*-pyran (**2**)), and the product was identical with that obtained with **3** and the amine. The reduction with this amine seems to be general, since 2,6-diphenylpyrilium perchlorate also gave 2,6-diphenyl-4*H*-pyran (**8**) in 36% yield (also see the results with xanthylium perchlorate below). We have not thoroughly investigated different amines, but triethylamine and methyl-dicyclohexylamine reduced **1** in 35% and 43% yield, respectively.



We showed previously that xanthylium perchlorate did not give a dimer by the method shown in Scheme I (1). In

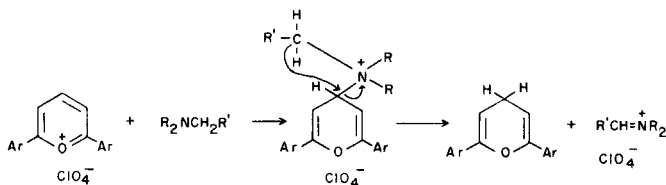




this case the triphenylphosphonium salt **9** is formed, but it does not react with pyridine. Treatment of **9** with a tertiary amine gave xanthene (**10**), which was also obtained from xanthylum perchlorate and a tertiary amine.

We can only speculate about the mechanism of these reductions by a tertiary amine. The source of the hydrogen is the amine because no deuterated product is obtained when the reaction is carried out in deuterioacetonitrile. One possible mechanism involves an intramolecular hydride transfer as shown in Scheme II.

Scheme II



The reaction of the phosphonium salt **9** with the amine could be the result of an equilibrium of **9** with xanthylum perchlorate followed by the reaction of the latter as shown in Scheme II.

The method shown in Scheme I did not work with 2,6-di(*t*-butyl)pyrylium perchlorate (**11**) (1) because **11** did not react with triphenylphosphine. Compound **11** did react with tributylphosphine to give the phosphonium salt **12**, but treatment of **12** with diisopropylethylamine gave no reaction. The base sodium bis(trimethylsilyl)amine was allowed to react with **11** in refluxing toluene. Tlc analysis of the reaction mixture (silica gel, dichloromethane) showed four spots which were approximately equal in intensity. None of these spots corresponded to an *R<sub>f</sub>* value predicted for the dimer (all dimers investigated to date move at or near the solvent front in dichloromethane).

## EXPERIMENTAL

Melting points were determined with a Mel-Temp apparatus and are uncorrected. The nmr spectra were recorded in deuteriochloroform on a Varian EM-390 spectrometer with TMS as internal standard. 2,6-Diphenylpyrylium perchlorate was prepared by the published procedure (2). However, when this procedure was used to prepare the dianisylpyrylium salt **3**, the product was contaminated with up to 20% of 1,3-di(4-methoxyphenyl)benzene. The preparation of pure **3** is therefore included.

### 2,6-Di(4-methoxyphenyl)pyrylium Perchlorate (3).

To a stirred mixture of 30 g (0.2 mole) of *p*-methoxyacetophenone and

100 ml of triethyl orthoformate was added 25 ml of 70% perchloric acid at a rate to maintain the temperature of the reaction mixture at 30-35°. The mixture was stirred overnight, and the solid was collected and washed with acetic acid and then ether. This material could not be purified by repeated recrystallizations from various solvents (as shown by the presence of two methoxy groups in the nmr and poor elemental analysis), but the impurity was readily removed by extracting the crude product with toluene in a Soxhlet extractor for 24 hours; yield 20 g; mp 275-276°.

*Anal.* Calcd. for  $C_{19}H_{17}ClO_3$ : C, 58.1; H, 4.4; Cl, 9.0. Found: C, 57.8; H, 4.1; Cl, 8.8.

### Tributyl-4-(2,6-diphenyl)-4*H*-pyran-4-yl Phosphonium Perchlorate.

A mixture of 1.7 g of the pyrylium salt **1** and 1.0 g of the phosphine **4** in 25 ml of pyridine was stirred under nitrogen for 2 hours. The solution was chilled, and the white solid was collected; yield 2.1 g (78%); mp 200-201°.

*Anal.* Calcd. for  $C_{29}H_{40}ClO_3P$ : C, 65.0; H, 15.0; P, 8.9. Found: C, 65.0; H, 14.8; P, 9.0.

### 2,2',6,6'-Tetraphenyl- $\Delta^{4,4'}$ -bi-4*H*-pyran (2).

A mixture of 1.0 g of the phosphonium salt, 2 ml of diisopropylethylamine, and 25 ml of acetonitrile was refluxed for 2 hours. An orange-red color developed, and a crystalline solid separated. The mixture was cooled to room temperature, and the solid was collected; yield 0.43 g (100%); mp 319-320°. The ir spectrum was identical with that of a sample prepared by another method (1).

### Tributyl-4-[2,6-di(4-methoxyphenyl)]-4*H*-pyran-4-yl Phosphonium Perchlorate (5).

A mixture of 1.8 g of the pyrylium salt **3** and 0.93 g of tributylphosphine in 25 ml of acetonitrile was stirred for 2 hours under nitrogen. The solution was concentrated and diluted with ether, and the solid was collected; yield 2.55 g (93%); mp 165-166°. The nmr spectrum shows butyl groups at  $\delta$  ppm 0.9 (m, 9H), 1.48 (m, 12H), and 2.2 (m, 6H);  $CH_3O$  at 3.82 (s, 6H); H4 at 4.45 (quintet, 1H); H3, 5, 5.35 (quartet, 2H), and aromatics 6.87 (d, 4H) and 7.5 (d, 4H).

*Anal.* Calcd. for  $C_{31}H_{44}ClO_4P$ : C, 62.4; H, 7.4; P, 5.2. Found: C, 62.1; H, 7.4; P, 5.4.

### 2,2',6,6'-Tetra(4-methoxyphenyl)- $\Delta^{4,4'}$ -bi-4*H*-pyran (6).

A mixture of 1.3 g (2.18 mmole) of **5**, 2 ml of diisopropylethylamine, and 25 ml of acetonitrile was refluxed for 4 hours; the mixture was chilled, and the solid was collected; yield 0.52 g (81%); mp 307-308°. The product darkened about 100° below the mp, and the color changed from pale brown to dark red when the solid was rubbed on a clay plate or when a potassium bromide pressing was prepared. The mass spectrum shows *m/e* 584, 569, 568, 449, 292, 135, 91 and 77.

*Anal.* Calcd. for  $C_{38}H_{38}O_6$  (584): C, 78.1; H, 5.5. Found: C, 78.2; H, 5.6.

### 2,6-Di(4-methoxyphenyl)-4*H*-pyran (7).

A mixture of 1.8 g of the pyrylium salt **3**, 100 mg of tributylphosphine, 2 ml of diisopropylethylamine, and 25 ml of acetonitrile was refluxed for 4 hours. The solution was chilled and the solid was collected. The solid was chromatographed (silica gel, dichloromethane) to give 0.52 g (37%) of yellow, air-sensitive product; mp 84-85°. The nmr spectrum shows H4 at  $\delta$  ppm 2.98 (t, 2H, *J* = 4 Hz);  $OCH_3$ , 3.77 (s, 6H); 3H 5.29 (t, 2H, *J* = 4 Hz); and aromatics as 2 doublets at 6.76, 6.88 and 7.45, 7.57 (8H). The

mass spectrum shows *m/e* 294, 293, 145, 135, 121, 87, 77, 63, 51 and 39. We did not run an elemental analysis because the compound was not stable.

Compound **7** was also prepared by stirring a mixture of 1 g of **3**, 2 ml of diisopropylethylamine, and 15 ml of acetonitrile for 4 hours at room temperature and working up as described above; yield 0.45 g (60%), with nmr and ir spectra identical with those of the other sample.

A third method for the preparation of **7** consisted of stirring a mixture of 1 g of **3** and 0.25 g of sodium borohydride in 25 ml of isopropyl alcohol for 3 hours, diluting with 5 ml of water, and collecting the solid. The solid was chromatographed as before, yielding 0.6 g (81%) of **7**.

#### 2,6-Diphenyl-4*H*-pyran (**8**).

A mixture of 2 g of the pyrilium salt **1**, 4 ml of diisopropylethylamine, and 25 ml of acetonitrile was stirred for 3 hours and evaporated, and the residue was chromatographed on silica gel (hexane/dichloromethane, 3:1); yield 0.5 g (36%) of air-sensitive material. The ir and nmr spectra of the product were identical with those of a sample prepared by the published procedure (2).

The same procedure was used substituting 5 ml of triethylamine or 4 ml of dicyclohexylethylamine for diisopropylethylamine, giving **8** in yields of 0.49 g (35%) and 0.60 g (43%), respectively.

#### Xanthene (**10**).

A mixture of 0.54 g of the phosphonium salt **9**, 1 ml of diisopropylethylamine, and 10 ml of pyridine was refluxed for 1 hour and then

evaporated to dryness. The glassy residue was stirred with methyl alcohol, giving a white solid which was shown to be triphenylphosphine. The alcohol solution was evaporated to dryness, and the residue was chromatographed on silica gel (eluted with hexane), giving 102 mg (56%) of **10** which was identical with an authentic sample (ir, tlc).

The reaction was repeated with 0.56 g. of xanthylum perchlorate, giving 204 mg (57%) of **10**.

#### Tributyl-4-[2,6-di(*t*-butylphenyl)]-4*H*-pyran-4-yl Phosphonium Perchlorate (**11**).

Compound **11** was prepared by the procedure described for the preparation of **5**; yield 82%; mp 135-136°. The nmr spectrum shows  $\delta$  ppm H3, 4.58 (two doublets, 2H); H4, 4.09 (quintet, 1H); *n*-butyl, 2.18 (m, 6H), 1.50 (m, 12H), 1.00 (m, 9H); *t*-butyl, 1.11 (s, 18H).

*Anal.* Calcd. for C<sub>22</sub>H<sub>48</sub>ClO<sub>3</sub>P: C, 60.7; H, 9.7; P, 6.3. Found: C, 60.4; H, 9.5; P, 6.6.

#### REFERENCES AND NOTES

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