°C (2.5 mm); IR 3400 (OH), 1640 and 1605 (C=C), 1460, 1376, 1120, 985 and 892 (CH_2=CH); NMR 0.90 (t, J = 7 Hz, 3 H, CH_3CH_2), 1.14 (s, 3 H, CH_3COH), 1.2–1.7 (m, 4 H, $CH_2C(OH)CH_2$), 1.74 (s, 3 H, CH_3C=), 1.8–2.5 (m, 2 H, =$CHCH_2$), 4.85 (d, J = 6 Hz, 1 H, cis =CH_2), 5.00 (d, J = 17 Hz, 1 H, trans =CH_2), 5.42 (t, J = 6 Hz, 1 H, CH_2CH=), 6.29 and 6.75 ppm (2 q, J = 9 and 17 Hz, 1 H, CH=CH_2); MS m/e 168 (parent), 151 ($C_{11}H_{19}$, M - OH), 150 ($C_{11}H_{18}$, M - H_2O), 121 (C_9H_{13}), 93 (C_7H_9), 81 (C_6H_9), 73 (C_4H_9O), 68 (C_5H_8).

6-Chloro-3-methyl-2-hexene (8a) and 6-Chloro-3-methyl-3-hexene (8b). 6-Chloro-3-methyl-3-hexanol (**7**) was prepared by a method similar to that described for the preparation of **2**: yield 65%, bp 71–73 °C (2 mm). A mixture of **7** (45.2 g, 0.30 mol) and concentrated HCl (50 mL) was stirred for 1 h at room temperature. The solution was extracted with ether, and the extract was washed with 5% sodium carbonate solution and water. After evaporation of ether under reduced pressure, DMF (50 mL) was added, and the mixture was heated at 130 °C for 3 h. Water was then added to the solution, and it was extracted with ether. The ether solution was dried over sodium sulfate and concentrated in vacuo. Subsequent distillation under reduced pressure afforded a mixture of **8a** and **8b**: 75% yield, bp 70–73 °C (35 mm).

An authentic sample of **8a** was prepared by the Wittig reaction of **1** with ethylidenetriphenylphosphorane. Thus, to a mixture of ethyltriphenylphosphonium bromide (72.5 g, 0.20 mol) with ether (500 mL) was added under nitrogen a 15% hexane solution of n-butyllithium (0.20 mol), and the mixture was stirred for 3 h at room temperature. **1** was then added dropwise at room temperature, and the mixture was refluxed for 2 h. Water was added to stop the reaction, and the mixture was extracted with hexane. After the solution was dried over sodium sulfate, ether and hexane were evaporated under reduced pressure, and the distillation of the residual oil afforded pure **8a** in 20% yield: bp 64–65 °C (23 mm); IR 1670 (C=C), 1440, 1380, 1260, 1015, 808 (CH=C); NMR 1.4–1.8 (several s, 6 H, CH_3C=), 1.8–2.3 (m, 4 H, CH_2CH_2C=), 3.45 (t, J = 6 Hz, 2 H, CH_2Cl), 5.0–5.5 ppm (m, 1 H, =CH); MS m/e 134 and 132 (parent), 83 (C_6H_{11}), 69 (C_5H_9).

2,6-Dimethyl-5-octen-2-ol (Dihydroalloocimenol, 9a) and 2,6-Dimethyl-6-octen-2-ol (9b). A mixture of **9a** and **9b** was obtained in 76% yield by a reaction of **8a** and **8b** with acetone similar to that described for the preparation of **4**: bp 69–71 °C (2 mm); IR 3390 (OH), 1670 (C=C), 1470, 1380, 1200, 1150, 905; NMR 0.89 (t, J = 6 Hz, CH_2CH_3), 1.18 (s, CH_3COH), 1.2–1.7 (m, CCH_2C), 1.60 (s, CH_3C=), 1.7–2.3 (m, CH_2C=), 4.8–5.3 ppm (m, CH=); MS m/e 138 ($C_{10}H_{18}$, M - H_2O), 123 (C_9H_{15}), 95 (C_7H_{11}), 83 (C_6H_{11}), 69 (C_5H_9), 68 (C_5H_8), 59 (C_3H_7O).

Similarly, 7-methyl-6- or -7-nonen-3-ol (**10**) and 3,7-dimethyl-6- or -7-nonen-3-ol (**11**) were obtained by the reactions of **8** with propionaldehyde and methyl ethyl ketone, respectively. Yield of **10** was 55%: bp 79–82 °C (3 mm); 3350 (OH), 1660 (C=C), 1450, 1370, 1110, 960; NMR 0.90 (t, J = 7 Hz, CH_3CH_2CHOH), 0.95 (t, J = 7 Hz, CH_3CH_2C=), 1.2–1.7 (m, CCH_2C), 1.58 (s, CH_3C=), 1.7–2.3 (m, CH_2C=), ca. 3.3 (m, CHOH), 4.8–5.3 ppm (m, CH=); MS m/e 156 (parent), 139 ($C_{10}H_{19}$, M - OH), 138 ($C_{10}H_{18}$, M - H_2O), 127 ($C_8H_{15}O$), 95 (C_7H_{11}), 83 (C_6H_{11}), 69 (C_5H_9), 68 (C_5H_8), 59 (C_3H_7O). Yield of **11** was 70%: bp 79–81 °C (1 mm); IR 3420 (OH), 1670 (C=C), 1450, 1370, 1175, 1140, 925; NMR 0.86 (t, J = 7 Hz, CH_3CH_2COH), 0.96 (t, J = 7 Hz, CH_3CH_2C=), 1.10 (s, CH_3COH), 1.2–1.7 (m, CCH_2C), 1.58 (s, CH_3C=), 1.7–2.3 (m, CH_2C=), 4.8–5.3 ppm (m, CH=); MS m/e 152 ($C_{11}H_{20}$, M - H_2O), 123 (C_9H_{15}), 95 (C_7H_{11}), 83 (C_6H_{11}), 73 (C_4H_9O), 69 (C_5H_9).

When n-propyl bromide, n-butyl chloride, isoamyl chloride, or n-hexyl chloride were used in place of ethyl bromide in the reaction with **1**, subsequent dehydration and Grignard reaction with acetone gave alkyl substituted dihydroalloocimenol and their isomers, $(CH_3)_2C(OH)(CH_2)_3C(CH_3)$=$CHCH_2R$ and $(CH_3)_2C(OH)(CH_2)_2CH$=$C(CH_3)(CH_2)_2R$. The substituent R, yield, boiling point, and mass spectral fragments are as follows: CH_3, 68%, 78–80 °C (2 mm), MS m/e 152 ($C_{11}H_{20}$, M - H_2O), 137 ($C_{10}H_{17}$), 109 (C_8H_{13}), 97 (C_7H_{13}), 95 (C_7H_{11}), 83 (C_6H_{11}), 69 (C_5H_9), 68 (C_5H_8), 59 (C_3H_7O); C_2H_5, 70%, 92–94 °C (2 mm), MS m/e 166 ($C_{12}H_{22}$, M - H_2O), 151 ($C_{11}H_{19}$), 123 (C_9H_{15}), 95 (C_7H_{11}), 69 (C_5H_9), 68 (C_5H_8), 59 (C_3H_7O); $(CH_3)_2CH$, 67%, 100–103 °C (2 mm), MS m/e 180 ($C_{13}H_{24}$, M - H_2O), 165 ($C_{12}H_{21}$), 137 ($C_{10}H_{17}$), 95 (C_7H_{11}), 69 (C_5H_9), 68 (C_5H_8), 59 (C_3H_7O); $CH_3(CH_2)_3$, 65%, 109–113 °C (2 mm), MS m/e 194 ($C_{14}H_{26}$, M - H_2O), 179 ($C_{13}H_{23}$), 139 ($C_{10}H_{19}$), 123 (C_9H_{15}), 95 (C_7H_{11}), 69 (C_5H_9), 68 (C_5H_8), 59 (C_3H_7O).

Hydroxygeranyl Ethyl Ether (12). A mixture of **2** (0.30 mol) and 47% HBr solution (80 mL) was stirred at room temperature for 3 h. The mixture was extracted with ether, and the ether solution was washed with water and dried over sodium sulfate. After evaportion of the ether, distillation gave 1-bromo-6-chloro-3-methyl-2-hexene in 60% yield; bp 84–86 °C (1 mm). The bromide was added to a solution of sodium (0.16 mol) in ethanol (150 mL), and the solution was stirred at room temperature for 2 h. After evaporation of ethanol, the mixture was extracted with ether, and the extract was washed with water and dried over sodium sulfate. The ether was evaporated off, and the distillation of the residue gave 6-chloro-1-ethoxy-3-methyl-2-hexene in 85% yield: bp 79–81 °C (1 mm); IR 1670 (C=C), 1436, 1372, 1100 (C–O–C); NMR 1.14 (t, J = 7 Hz, 3 H, CH_3CH_2), 1.64 and 1.72 (2 s, 3 H, CH_3C=), 1.7–2.4 (m, 4 H, $ClCH_2CH_2CH_2$), 3.37 (q, J = 7 Hz, 2 H, OCH_2CH_3), 3.46 (t, J = 7 Hz, 2 H, $ClCH_2$), 3.86 (d, J = 6 Hz, 2 H, =$CHCH_2O$), 5.33 ppm (t, J = 7 Hz, 1 H, =CH).

The Grignard reaction of 6-chloro-1-ethoxy-3-methyl-2-hexene with acetone was carried out in a similar manner to that for **4**, and **12** was obtained in 70% yield: bp 102–103 °C (1 mm); IR 3420 (OH), 1662 (C=C), 1450, 1370, 1095 (C–O–C); NMR 1.14 (s, 6 H, CH_3COH), 1.14 (t, J = 7 Hz, 3 H, CH_2CH_3), 1.3–1.6 (m, 4 H, $CH_2CH_2CH_2C$=), 1.8–2.3 (m, 2 H, CH_2C=), 3.39 (q, J = 7 Hz, 2 H, OCH_2CH_3), 3.89 (d, J = 7 Hz, 2 H, =CCH_2O), 5.30 ppm (t, J = 7 Hz, 1 H, =CH); MS m/e 182 ($C_{12}H_{22}O$, M - H_2O), 167 ($C_{11}H_{19}O$), 139 ($C_9H_{15}O$), 137 ($C_{10}H_{17}$), 113 ($C_7H_{13}O$), 99 ($C_6H_{11}O$), 69 (C_5H_9), 68 (C_5H_8), 59 (C_3H_7O).

Registry No. 1, 5891-21-4; **2**, 42448-57-7; *cis*-**3a**, 61432-63-1; *trans*-**3a**, 42448-59-9; **3b**, 26831-14-1; *cis*-**4**, 7643-59-6; *trans*-**4**, 7643-60-9; *cis*-**5**, 71616-37-0; *trans*-**5**, 71616-38-1; *cis*-**6**, 71616-39-2; *trans*-**6**, 71616-40-5; **7**, 71616-41-6; **8a**, 60379-90-0; **8b**, 71616-42-7; **9a**, 59861-43-7; **9b**, 30385-25-2; **10**, 71616-23-4; **11**, 71616-25-6; **12**, 71616-43-8; α-acetyl-γ-butyrolactone, 517-23-7; vinyl bromide, 593-60-2; acetone, 67-64-1; propionaldehyde, 123-38-6; methyl ethyl ketone, 78-93-3; ethyltriphenylphosphonium bromide, 1530-32-1; n-propyl bromide, 106-94-5; n-butyl chloride, 109-69-3; isoamyl chloride, 107-84-6; n-hexyl chloride, 544-10-5; ethyl bromide, 74-96-4; 2,6-dimethyl-5-nonen-2-ol, 71616-44-9; 2,6-dimethyl-5-decen-2-ol, 71616-45-0; 2,6,9-trimethyl-5-decen-2-ol, 71616-46-1; 2,6-dimethyl-5-dodecen-2-ol, 71616-47-2; 2,6-dimethyl-6-nonen-2-ol, 71616-48-3; 2,6-dimethyl-6-decen-2-ol, 71616-49-4; 2,6,9-trimethyl-6-decen-2-ol, 71616-50-7; 2,6-dimethyl-6-dodecen-2-ol, 71616-51-8; 1-bromo-6-chloro-3-methyl-2-hexene, 71616-52-9; 6-chloro-1-ethoxy-3-methyl-2-hexene, 71616-53-0.

Synthesis of Certain Bipyranylidene and Bi(thiopyranylidene) Derivatives

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Since the first report on the high electrical conductivity of the charge-transfer salt of tetrathiafulvalene–tetracyanoquinodimethane (TTF–TCNQ),[1] there has been much interest in the synthesis of tetrathiafulvalene (TTF) and its derivatives and analogues. We have been interested in the synthesis of 2,2',6,6'-tetraaryl-4,4'-bipyranylidenes, the sulfur analogues, and related compounds, as this type of compound also forms highly conducting salts with TCNQ.[2]

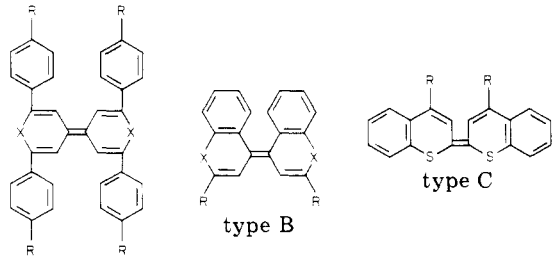
These dimers are prepared by heating a 4*H*-pyran-4-thione or a 4*H*-4,4-dichloropyran with copper in a solvent

(1) Ferris, J. P.; Cowan, D. O.; Walatka, V., Jr.; Perlstein, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 948.

(2) Alizon, J.; Gallice, J.; Robert, H.; Delplanque G.; Weyl, C.; Fabre, C.; Strzelecka, H. *Mol. Cryst. Liq. Cryst.* **1976**, *32*, 157.

0022-3263/79/1944-4456$01.00/0

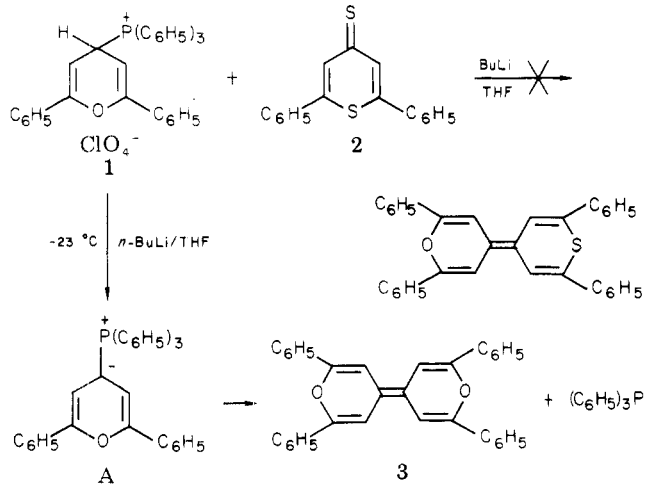
Table I. Pyranylidene and Thiopyranylidene Dimers



compd	type	X	R	yield, %	mp, °C	anal. (calcd/found) C	H	other
3	A	O	H	87	318-320[a]			
5	A	S	H	71	322-323[b]			
6	A	O	Cl	50	392-393	67.8	3.3	Cl 23.5
						67.7	3.7	23.4
7	A	O	CH_3	44	352-353	87.7	6.2	
						87.5	6.3	
8	B	O	C_6H_5	72	226-227[c]			
9	C		C_6H_5	88	288-289	81.0	4.5	S 14.4
						80.7	4.2	14.7
10	C		H	45	188-190	73.8	4.1	
						73.4	3.9	
11	B	S	H	17	240-241	73.8	4.1	
						73.6	3.9	

[a] Lit.[9] mp 320-323 °C. [b] Lit.[9] mp 322-324 °C. [c] Lit.[10] mp 226 °C.

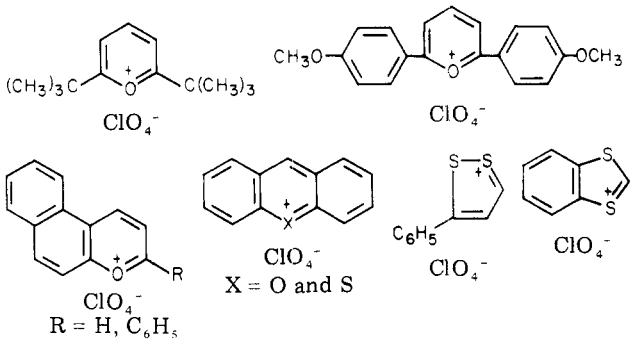
such as xylene,[3] by treating a 4*H*-pyran-4-one with zinc in acidic media,[3] and by reacting a pyrylium salt and zinc in acetonitrile.[4] While attempting to prepare unsymmetrical dimers, we found a new and convenient method for preparing symmetrical dimers. We were investigating the addition of the thiopyran-4-thione **2** to the Wittig reagent prepared from the phosphonium salt **1** and 1 equiv of *n*-BuLi in THF at ca. −23 °C. From this reaction, which



was slowly equilibrated to ambient temperature overnight under nitrogen, we isolated only the symmetrical dimer **3** and recovered quantitatively the unreacted **2**. This result implies that **1** with a suitable base yields a Wittig intermediate A which on warming couples to give **3** and triphenylphosphine and suggested the method of synthesis described in this paper.

2,6-Diphenylpyrylium perchlorate (**4**) or fluoroborate and a catalytic amount (10% by weight is a convenient quantity) of triphenylphosphine in pyridine on heating on a steam bath for 2 h gave the dimer **3** in 87% yield. This reaction is similar to that reported by Märkl et al., who prepared **3** from **4** and an equimolar amount of trimethylolphosphine in refluxing pyridine,[5] but our method is more convenient and does not require the potentially dangerous trimethylolphosphine.

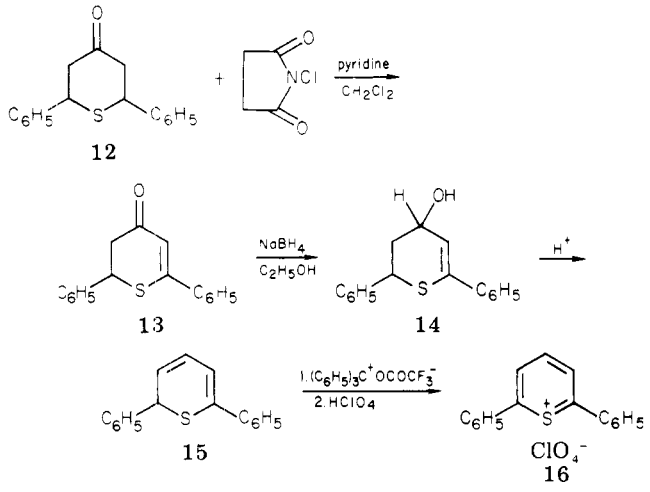
The scope of the reaction was investigated, and Table I lists the compounds that were prepared. Equally interesting are the compounds that did not yield dimers under these reaction conditions. The following compounds did not give the dimer.



From these data, it appears that the method is suitable for the preparation of dimers from flavylium salts and from 2,6-diarylpyrylium and thiopyrylium salts which do not contain strong electron-donating groups. The first three pyrylium salts did not give a dimer because they did not form a phosphonium salt with triphenylphosphine. Xanthylium perchlorate gave a phosphonium salt which remained unchanged in refluxing pyridine. The failure of the dithiolium salts to give the dimer was not investigated. The assignment of structures **10** and **11** to the dimers isolated from the reaction of benzo[*b*]pyrylium perchlorate with triphenylphosphine is only tentative and is based on the known greater reactivity of the 2-position of the pyry-

(3) Schönberg, A.; Asker, W. *Chem. Rev.* **1945**, *37*, 1.
(4) Fabre, C.; Fugnitto, R.; Strzelecka, H. *C. R. Ser. C Hebd. Seances Acad. Sci.*, **1976**, *282*, 175.
(5) Märkl G.; Fischer, D.; Olbrich, H. *Tetrahedron Lett.* **1970**, 645.

Scheme I



lium salt, and the compound formed in the largest yield was given structure **10**. When a solution of **4** in pyridine was heated on a steam bath, **3** was not formed. The dimer **3** can be prepared from the phosphonium salt **1** and hot pyridine, but this method offers no advantages.

The starting pyrylium salts are conveniently prepared by the method of Dorofeenko and Mezheritskii[6] by adding perchloric acid to a methyl aryl ketone in excess triethyl orthoformate. For the preparation of larger amounts of the pyrylium salt, where the use of large quantities of perchloric acid could be hazardous, anhydrous fluoroboric acid in acetic acid gave the pyrylium fluoroborate salts in good yield. The preparation of 2,6-diphenylthiopyrylium perchlorate is outlined in Scheme I.

Experimental Section

Melting points were determined on a Mel-Temp apparatus and are uncorrected. The dimers **3**, **5**, and **7** were prepared by published procedures and showed infrared spectra identical with those of the compounds prepared in this paper. The other dimers gave satisfactory elemental analyses. The mass spectra of all the dimers gave an M^+. We had trouble determining the NMR spectra because of the poor solubility of the dimers.

General Method for the Preparation of Dimers. A mixture of 10 mmol of the pyrylium or thiopyrylium salt, 10 wt % of triphenylphosphine, and 15 mL of pyridine was heated on a steam bath for 2 h and chilled. The solid was collected and recrystallized from pyridine.

Reaction of Benzo[*b*]thiopyrylium Perchlorate. A mixture of 1.0 g of benzo[*b*]thiopyrylium perchlorate, 0.1 g of triphenylphosphine, and 5 mL of pyridine was heated on a steam bath for 1 h and chilled. The red solid was collected and recrystallized from pyridine to yield 0.095 g of **11**: mass spectrum, *m/e* 292, 260, 259, 258, 178, 146, 93.

The mother liquors were diluted with methyl alcohol, and the solid was collected and recrystallized twice from a mixture of pyridine and methyl alcohol. The mass spectrum of this material (**10**) gives mostly *m/e* 292 (M^+), but small amounts of *m/e* 438 and 582 were present. The infrared spectra of **10** and **11** were different.

2,6-Diphenylpyrylium Fluoroborate. To 100 mL of acetic anhydride at −10 °C was added 33.3 g of 48% fluoroboric acid, keeping the temperature at 5–15 °C. This solution was added dropwise over 30 min at ambient temperature to a mixture of 23 mL of acetophenone and 100 mL of triethyl orthoformate. The mixture was stirred for 2 h and allowed to stand overnight. The yellow solid was collected and washed with ether: yield 20.2 g; mp 210–212 °C. Anal. Calcd for $C_{17}H_{13}BF_4O$: C, 63.8; H, 4.1. Found: C, 63.6; H, 3.8.

(6) Mezheritskii, V.; Dorofeenko, G. *Zh. Org. Khim.* **1967**, *3*, 1533. Zhungietu, G.; Lazur'evskii, G. *Zh Vses. Khim. Ova.* **1968**, *13*, 597.

2,6-Diphenylthiopyrylium Perchlorate (16). A mixture of 13.2 g (0.05 mol) of 2,6-diphenyl-2,3-dihydro-4*H*-thiopyran-4-one (**13**),[7] 200 mL of ethanol, and 2 g of $NaBH_4$ was stirred for 1 h and then diluted with water, and the gummy solid was collected. The solid was dissolved in ether, washed with water, and dried ($MgSO_4$), and the solvent was removed, giving 12 g of **14**. Anal. Calcd for $C_{17}H_{16}OS$: C, 76.1; H, 6.0; S, 11.9. Found: C, 75.8; H, 5.8; S, 11.9.

A mixture of 20 g of **14**, 1 g of *p*-toluenesulfonic acid, and 250 mL of toluene was refluxed for 1 h, and the toluene was removed on a rotary evaporator. The residue was dissolved in ether and passed through a short column of alumina. Evaporation of the solvent gave 14 g of **15**.

A mixture of 5.8 g (0.023 mol) of **15**, 6 g (0.023 mol) of triphenylmethanol, and 20 mL of trifluoroacetic acid was refluxed for 2 h, and the solvent was removed under vacuum. The residue was dissolved in ether and ethanol, and 3.5 mL of 70% perchloric acid was added. The mixture was chilled, and the solid was collected. The solid was stirred with 75 mL of boiling benzene and filtered hot. This was repeated twice, giving 6.1 g (83%) of **16**, mp 185–186 °C (lit.[8] mp 185–186 °C).

Registry No. **3**, 42506-57-0; **5**, 42506-60-5; **6**, 71750-02-2; **7**, 59155-88-3; **8**, 4388-05-0; **9**, 71750-03-3; **10**, 71750-04-4; **11**, 71785-23-4; **13**, 60839-95-4; **14**, 71750-05-5; **15**, 71750-06-6; **16**, 13586-29-3; benzo[*b*]thiopyrylium perchlorate, 3220-72-2; triphenylphosphine, 603-35-0; 2,6-diphenylpyrylium fluoroborate, 15696-48-7; acetophenone, 98-86-2; triethyl orthoformate, 122-51-0; 2,6-di-*p*-tolylpyrylium perchlorate, 55665-98-0; 2,6-bis(*p*-chlorophenyl)pyrylium perchlorate, 55666-00-7.

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(10) Bayer, E.; Kraener, G. *Chem. Ber.* **1964**, *97*, 1057.

Synthesis of 7,8-Epoxy-7,8-dihydroretinoids

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Of the various retinoid epoxides, only those in which the 5,6 double bond has been oxidized are well documented.[1-3] Recent assertions that retinol undergoes Co(II)-mediated autoxidation to give the 11,12-epoxide[4] or peracetic acid oxidation to give the 11,12-epoxy aldehyde[5] do not seem to be adequately documented and are inconsistent with subsequent experiments.[6] In connection with a project which is directed toward the preparation of possible retinoid metabolites, it is desirable to have samples of the various epoxides. Thus, we have resorted to total synthesis. In this Note we report the synthesis of 7,8-epoxy-7,8-dihydroretinoids **1**–**4**. We have also characterized the 13*Z* isomer of methyl 7,8-epoxy-7,8-dihydroretinoate (**5**).

Reaction of vinylmagnesium bromide with methyl (*E*)-3-formylbut-2-enoate[7] affords alcohol **7** in 83% yield. This

(1) P. Karrer and E. Jucker, *Helv. Chim. Acta*, **28**, 717 (1945); **30**, 559 (1947).
(2) F. B. Jungalwala and H. R. Cama, *Biochem. J.*, **95**, 17 (1965).
(3) K. V. John, M. R. Lakshanan, and H. R. Cama, *Biochem. J.*, **103**, 539 (1967).
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(6) S. C. Welch, private communication.

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