

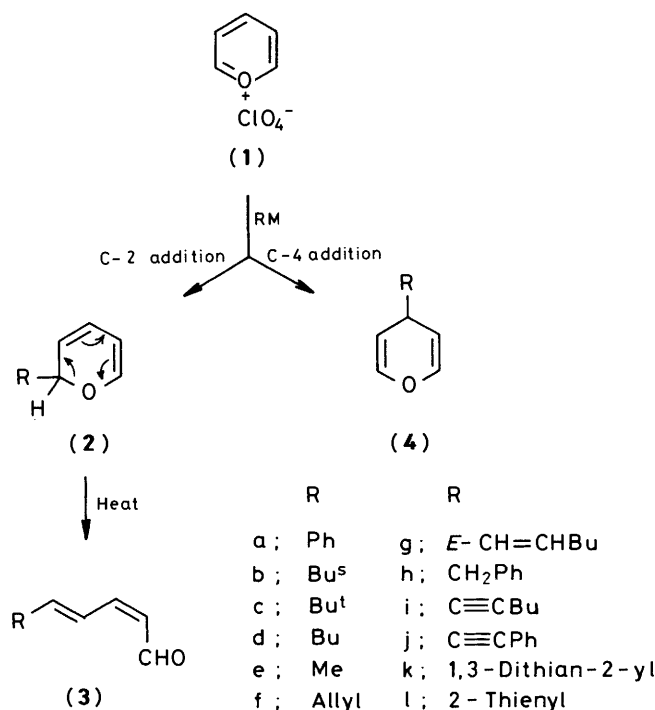
Stereoselective Synthesis of *Z,Z*, *4E*-Dienals by Addition of Organometallic Reagents to Pyrylium Perchlorate¹

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A facile and stereoselective approach to *Z,Z*, *4E*-dienals and derived products is presented. The method involves addition of an organometallic reagent to a pyrylium salt, followed by electrocyclic ring-opening of the intermediate *2H*-pyran, to give the desired *Z,E*-dienal, usually with greater than 95% stereochemical purity. These dienals may be trapped *in situ* with a second organometallic reagent, or oxidised or reduced, without loss of stereochemical integrity. The synthesis of (1,3*Z*,5*E*)-undeca-1,3,5-triene, a component of the essential oils of the brown Hawaiian seaweeds *Dictyopteris plagiogramma* and *D. australis*, is reported to illustrate the simplicity of the procedure.

In recent years, a great deal of attention has been devoted to the development of new, stereoselective approaches to conjugated polyenes, a class of compounds which includes natural products such as arachidonic acid metabolites² and insect pheromones.³ 2,4-Dienoic acids, dienals, dienols and their derivatives are useful starting materials for natural product syntheses and a variety of routes are available for the preparation of the *E,E*-, *E,Z*- and *Z,Z*-isomers.⁴ The number of procedures available for the stereoselective preparation of *Z,E*-dienoic acid derivatives is limited however,⁴⁻⁷ and to our knowledge there are no reported examples of their direct preparation from organometallic reagents by a five-carbon homologation process. We required such a procedure for the preparation of *Z,E*-dienals for leukotriene synthesis¹ and decided to explore the utility of pyrylium salts as the electrophilic component in these reactions. Organometallic addition at C-2 of the pyrylium cation (1) would give the 2-substituted *2H*-pyran (2) which would be expected^{8,9} to rearrange to the isomeric dienals (3) at room temperature or below¹⁰ in a stereospecific process as shown in Scheme 1. Addition to C-4 of the pyrylium cation, on the other



Scheme 1.

Table 1. Reactions of pyrylium perchlorate (1) with a range of phenyl organometallic reagents

Organometallic reagent	% Yield of dienal (3a) (<i>Z,E</i> : <i>E,E</i>) ^a	% Yield of pyran (4a)
PhLi	96 (ca. 97:3)	
PhMgBr	45 (ca. 86:14)	
Ph ₂ CuLi	7 (-) ^b	63
Ph ₄ Ti	75 (ca. 44:56)	
Ph ₄ Zr	24 (ca. 29:71)	

^a By ¹H n.m.r. spectroscopy (see text). ^b Not determined.

hand, would give the 4-substituted pyrans (4). There have been scattered reports of organometallic reactions with substituted pyrylium salts^{8,9,11,12} and addition to both C-2 and C-4 has been observed. In the absence of steric and electronic deactivation, addition to C-2 of the unsubstituted pyrylium cation would be expected to predominate^{8,9} although it has been stated that unsubstituted pyrylium cations 'do not give clean reactions, even with the most common nucleophiles such as ammonia.'⁹ Certainly, to our knowledge, no-one has looked at the organometallic addition reactions of unsubstituted pyrylium salts although the related addition of Grignard reagents to pyridine 1-oxide has been reported.⁷ We therefore set out to prepare pyrylium salts (1) and investigate their reactions with organometallic reagents (Tables 1 and 2).

The pyrylium cation has been isolated previously as its perchlorate,^{13,14} iodide,¹⁵ tetrachloroferrate,¹⁵ and tetrafluoroborate¹⁶ salts. Of the approaches reported to date, the most convenient appeared to be that of Klages and Träger,¹³ who treated sodium glutacetaldehyde dihydrate (readily prepared from pyridine 1-sulphonate)¹⁷ with perchloric acid, obtaining pyrylium perchlorate (1) in 83% yield. In our hands, this procedure proved to be straightforward and reliable although the yield was consistently much lower than that reported. We also prepared pyrylium tetrafluoroborate (from sodium glutacetaldehyde and ethereal tetrafluoroboric acid) and pyrylium iodide [from perchlorate salt (1) and hydriodic acid¹⁵] but in comparison trials with butyl-lithium the perchlorate salt (1) gave by far the best yields and so was adopted for this investigation. At this point it is pertinent to note that although compound (1) should be handled with care, being a potentially explosive perchlorate salt, we have experienced no problems of any kind in the preparation, purification, storage, or usage of this compound.

Stereoselective Preparation of Z,E-Dienals (3).—Pyrylium perchlorate (1), as a suspension in tetrahydrofuran (THF) or 1,2-

Table 2. Reactions of pyrylium salt (1) with organometallic reagents (RM)

RM	Dienal (3) (% Yield; Z,E: E,E) ^a	Pyran (4) (% yield)
BuLi	(3b) (81; ca. 97:3) ^b	
BuMgBr	(81; ca. 96:4)	
Bu ₂ CuLi	(24)	(4b) (41)
Bu ^o Li	(3c) (56; ca. 93:7)	
Bu ⁱ Li	(3d) (78)	
Bu ⁱ MgBr	(6; ca. 58:42)	
MeLi	(3e) (89)	
H ₂ C=CHCH ₂ Li	(3f) (24; ca. 74:26) ^c	(4f) (6)
H ₂ C=CHCH ₂ MgBr	(57)	(9)
(H ₂ C=CHCH ₂) ₂ CuMgBr	(48)	(12)
E-BuCH=CHAlBu ₂ BuLi (5) ^d	(3g) (64)	
PhCH ₂ Li	(3h) (27)	(4h) (41)
PhCH ₂ MgCl	(26)	(26)
(PhCH ₂) ₂ CuLi	(6)	(76)
BuC≡CLi	(3i) (86)	
PhC≡CLi	(3j) (65)	
1,3-Dithian-2-yl-lithium	(3k) (49; ca. 98:2)	(4k) (9)
2-Thienyl-lithium	(3l) (48; ca. 97:3)	

^a By ¹H n.m.r. spectroscopy (see text); no ratio is quoted if the Z,E-isomer alone was observed. ^b The yield dropped to 8% when pyrylium perchlorate (1) containing 3% ash by combustion analysis and no organic impurity according to ¹H n.m.r. spectroscopy was employed in the addition reaction. ^c The low yield of this product is almost certainly due to the difficulty of separating it from tetraphenyltin (see text). ^d Prepared from hex-1-yne by sequential treatment with DIBAL-H and BuLi.

dimethoxyethane, was treated with a variety of organometallic reagents at -78 °C and the products isolated (Tables 1 and 2). As the solubility of pyrylium perchlorate in either solvent is poor, initial experiments were conducted using hexamethylphosphoramide (HMPA) as co-solvent. However this proved to be superfluous and the yields obtained when HMPA was present were often inferior to those obtained in its absence. Preliminary experiments were carried out with phenyl organometallic reagents to determine the most suitable choice of metals for the reaction (Table 1).

As expected,^{8,9} addition to C-2 predominates resulting in the production of the required dienal (3a). The predictable exception (see later discussion) involved organocuprate addition, the pyran (4a) being the major product. The phenyl-lithium reaction exhibited high Z,E-stereoselectivity. Increasing amounts of the E,E-isomer were observed by ¹H n.m.r. spectroscopy as the metal was changed from lithium to magnesium, titanium, and zirconium. This poorer stereoselectivity presumably reflects the greater Lewis acidity of the metal ions concerned. The generality of these observations were demonstrated using a range of lithium, magnesium, and copper-based organometallics, as shown in Table 2.

The desired conjugated Z,E-dienals were obtained in fair to excellent yields (Table 2). It is important to note that the pyrylium perchlorate used in these reactions must be analytically pure (see Table 2, footnote b). The reaction is applicable to a range of organic moieties (primary, secondary, and tertiary alkyl, allyl, benzyl, alkynyl, vinyl, aryl, and heteroaryl). Yields of the product dienals were generally highest when organolithium reagents were used. Grignard reagents derived from primary alkyl halides gave yields comparable (better in the case of allyl) to the corresponding organolithium reagents but the results obtained with secondary and tertiary alkylmagnesium bromides and phenylmagnesium bromide were disappointing. The formation of (2Z,4E,6E)-undeca-2,4,6-trienal (3g) by treatment of

Table 3. ¹H N.m.r. shifts (J Hz) for formyl protons in the dienals (3)

	Observed		Literature E,E(J Hz)
	Z,E(J Hz)	E,E(J Hz)	
a	10.18 (7.5)	9.50(8)	9.51(7.5) ¹⁸ 9.55(8) ¹⁹
b	10.17(8)	9.53(7.5)	9.51(7.5) ¹⁸
c	10.18(7.5)	9.53(7.5)	
d	10.18(8)	9.55(8)	9.53(8) ²⁰
f	10.22(7.5)	9.56(7.5)	
k	10.09(7)	9.57(7.5)	
l	10.15(7.5)	9.50(7.5)	

pyrylium perchlorate with the aluminate reagent (5) is noteworthy as it provides a stereospecific route to Z,E,E-trienals directly from terminal acetylenes. In principle, the dienyne (3i) and (3j), prepared from the corresponding lithium alkynides, should also be useful triene precursors *via* subsequent alkyne reduction.

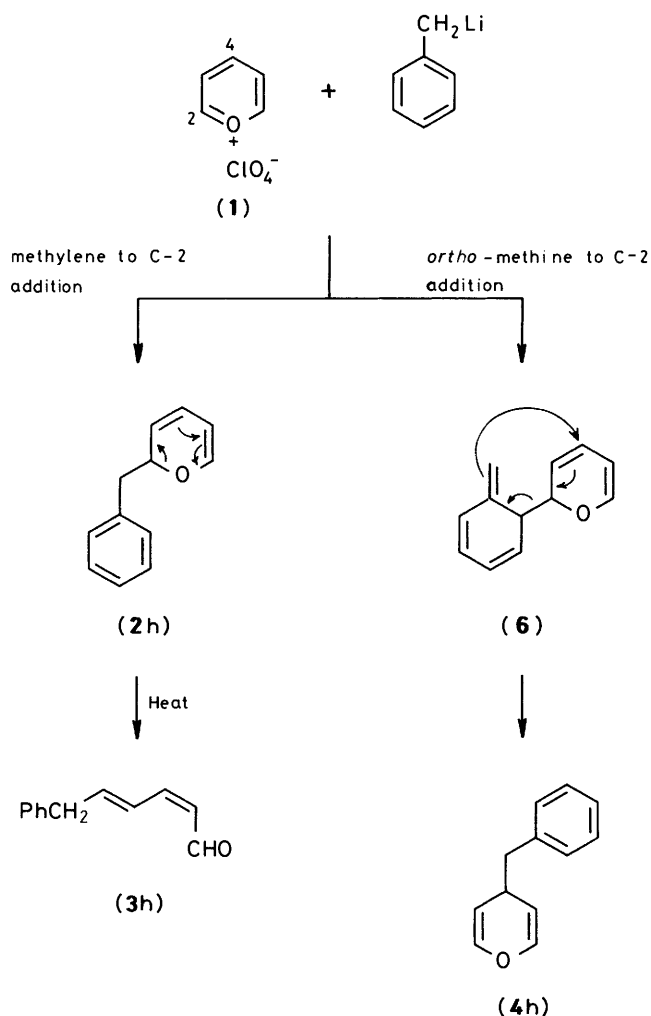
In general, the dienals (3) were obtained from organolithium reactions as essentially single isomers with ¹H n.m.r. characteristics consistent with the required Z,E-stereochemistry: where measured, the proton-proton coupling constants *J*_{2,3} lay in the range 10–12 Hz, and the corresponding values of *J*_{4,5} were consistently ca. 14.5 Hz. In some reactions, small quantities (up to 4%) of an isomeric dienal was produced as evidenced by the appearance of a second formyl proton resonance in the ¹H n.m.r. spectrum. Presumably, this minor product is the isomeric E,E-dienal formed by isomerisation during work-up. Support for this hypothesis comes from a comparison of observed and published n.m.r. data for the formyl chemical shift in dienals (Table 3).

The only organolithium reaction that proceeded with poor stereoselectivity involved the use of allyl-lithium, generated from tetra-allyltin and phenyl-lithium.²¹ The formation of a significant proportion of the E,E-isomer of the dienal (3f) presumably results from Lewis acid-catalysed isomerisation due to the presence of tin(IV) species, as the corresponding reaction with allylmagnesium bromide furnished isomerically pure material. The product Z,E-dienals also isomerise when heated or exposed to aqueous acid. For example, when the (2Z,4E)-nona-2,4-dienal (3b) was distilled (Kugelrohr), the ¹H n.m.r. spectrum of the distillate indicated the presence of ca. 15% of the E,E-isomer, and treatment of (3b) with 0.1 M hydrochloric acid in THF resulted in complete conversion into the E,E-isomer, although the product was accompanied by some polymeric material (no cyclopentenones were produced, in contrast to published results with a related dienal²²). Acid-catalysed isomerisation proceeds more cleanly in the case of (2Z,4E)-5-phenylpenta-2,4-dienal (3a), which was converted efficiently (95%) into the E,E-isomer under the same conditions. All of the dienals (3) proved stable to silica gel chromatography but few survived storage for more than 4 weeks, even at -20 °C. However, the readily formed dinitrophenylhydrazones were stable and provided additional confirmation of the product stereochemistry; the m.p.s for the dinitrophenylhydrazones derived from (3b) and (3e) were in agreement with published data⁷ and differed appreciably from those of the corresponding E,E-dinitrophenylhydrazones²³⁻²⁵ (see Experimental section).

In principle, both Z,E- and Z,Z-dienals could be produced by the thermally allowed disrotatory ring-opening of the intermediate 2H-pyran (2). The preference for the formation of the thermodynamically more favoured Z,E-isomer is consistent with literature precedent^{10,26} and with the formation of Z,E-dienal oximes, albeit in low yield, from the addition of Grignard reagents to pyridine 1-oxide.⁷

Formation of 4H-Pyrans (4).—Although the dienals (3) were usually the sole products isolated from addition of organolithium or Grignard reagents to pyrylium perchlorate, the 4H-pyrans (4) were isolated in three cases (Tables 1 and 2). When pyrylium perchlorate was treated with allyl-lithium, allyl-magnesium bromide or 2-lithio-1,3-dithiane, the expected *Z,E*-dienal (3) was formed along with small amounts (<10%) of the corresponding 4H-pyran (4). The allyl adducts (3f) and (4f) could not be separated but after standing for 2 weeks under nitrogen at -20°C , only the allylic dienal (3f) (and its *E,E*-isomer) could be detected by ^1H n.m.r. spectroscopy. This result would seem to indicate that under these conditions the 4H-pyran (4f) undergoes a slow Cope rearrangement to the corresponding 2H-pyran (2f) which ring-opens to give the dienal (3f). The slightly higher C-4 regioselectivity of the allyl and dithianyl reagents is consistent with the relatively 'soft' nature of these nucleophiles on the HSAB scale²⁷ and in accord with literature precedent.²⁸

The reaction of (1) with benzylmagnesium bromide produced considerable amounts of the pyran (4h) in addition to the dienal (3h), and with benzyl-lithium the pyran (4) was the major product. The increased proportion of C-4 addition with benzyl organometallics has precedent²⁹ but is surprising nonetheless. One possible explanation is that addition at the 2-position of the pyrylium cation still predominates but that a mixture of methylene and *ortho*-methine³⁰ coupled products, (2h) and (6), result as shown in Scheme 2.



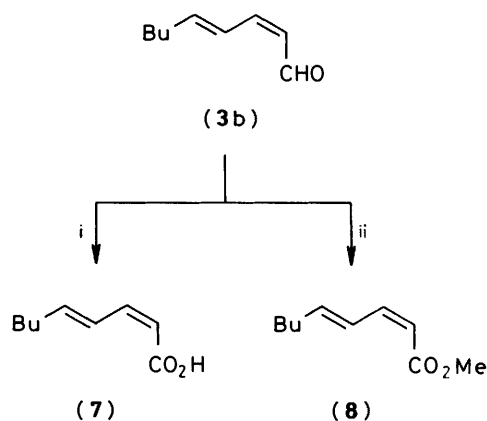
Scheme 2.

Subsequent Cope rearrangement of (6) would regenerate aromaticity in the phenyl ring producing the observed 4-benzylpyran (4h).

On the basis of these results, organocopper reagents would be expected to display an enhanced tendency to attack the pyrylium cation at C-4 and this proved to be the case (Tables 2 and 3), the 4H-pyrans (4) predominating from all of these reactions with the exception of that with diallylcopper magnesium bromide. The anomalous behaviour of allyl cuprates has been noted previously.³¹ More detailed studies of reactions between pyrylium salts and organocopper reagents have been reported recently.^{11,12}

Elaboration of the *Z,E*-Dienals (3).—Elaboration of the dienals (3) to the corresponding acids and alcohols can be achieved without loss of stereochemical integrity. Oxidation of the (*2Z,4E*)-nona-2,4-dienal (3b) with sodium chlorite³² gave the corresponding acid (7) whereas oxidation using manganese dioxide-sodium cyanide in methanol³³ gave the methyl ester (8).

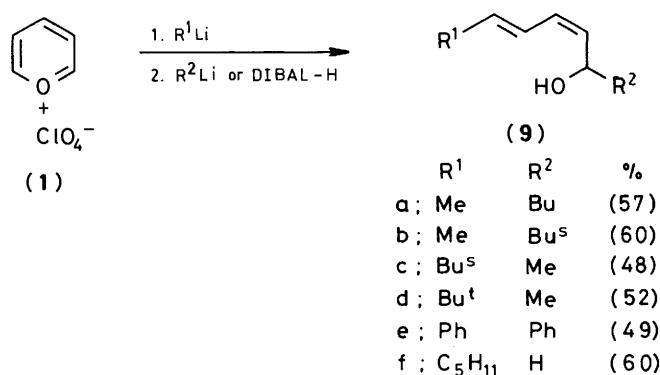
The *in situ*^{11,34} conversion of the dienals (3) into the corresponding primary or secondary alcohols (9) was also investigated as shown in Scheme 3. To aid this study an



Reagents: i, NaClO_2 , 2-methylbut-2-ene, Bu^iOH , KH_2PO_4 (91%); ii, MnO_2 , NaCN , MeOH (98%)

estimation was made of the temperature at which electrocyclic ring-opening (2)→(3) occurs at a reasonable rate. This was accomplished by treating a suspension of the pyrylium perchlorate (1) with an excess of butyl-lithium (3 equiv.) at -70°C and then allowing the mixture to warm to room temperature at a slow, controlled rate. Aliquots were removed after each 10°C increase in temperature and rapidly quenched with aqueous ammonium chloride. The *Z,E*-dienal (3b), formed by electrocyclic ring-opening after quenching, was the only product detected by t.l.c. at temperatures below -20°C . At -20°C , a more polar product, presumably the alcohol derived from addition of butyl-lithium to the dienal, was observed. At 0°C , t.l.c. analysis indicated that all of aldehyde (3b) had been consumed suggesting that electrocyclic ring-opening occurs at a reasonable rate within the range -20 to 0°C , which is consistent with published data.^{10,11,34} Therefore, solutions of 2H-pyrans (2), prepared by addition of 1 equiv. of organometallic reagent to pyrylium salt (1), as before, were allowed to warm to 0°C before being recooled to -78°C , and a second organometallic reagent added.

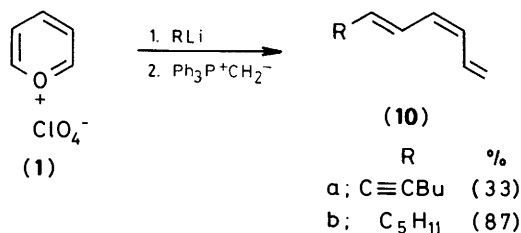
In this manner, the rearranged aldehydes (3) were converted *in situ* into secondary alcohols (9a–e) by further reaction with alkyl-lithium reagents and, in one instance, into the primary alcohol (9f) by reduction with di-isobutylaluminium hydride,



Scheme 3.

thereby providing a one-pot preparation of the 2*Z*,4*E*-dienols. Analysis of the dienol (**9f**) by 400 MHz n.m.r. spectroscopy confirmed the highly stereoselective nature of the reaction ($J_{2,3}$ 10 Hz, $J_{4,5}$ 15 Hz). The corresponding *E,E*-isomers were not detected in any of these reactions thereby demonstrating an advantage of the *in situ* procedure if the dienal (**3**) is prone to isomerisation on isolation.

This procedure also lends itself to the stereospecific preparation of trienes *via* Wittig reaction of the dienal (**3**). This strategy was applied to the synthesis of 1,3*Z*,5*E*-trienes; thus, treatment of pyrylium perchlorate (**1**) with hex-1-ynyl-lithium, and *in situ* trapping of the intermediate dienal (**3i**) with methylenetriphenylphosphorane gave the trienyne (**10a**) (Scheme 4). The



Scheme 4.

relatively low yield obtained for this transformation is not representative, as indicated by the efficient (87%) conversion of the pyrylium salt (**1**) into the (3*Z*,5*E*)-undeca-1,3,5-triene (**10b**), a component of the essential oils of the Hawaiian brown seaweeds *Dictyopteris plagiogramma* and *D. Australis*, by sequential treatment of the pyrylium perchlorate (**1**) with pentyl-lithium and methylenetriphenylphosphorane. In this reaction the Wittig reagent was added to the reaction mixture at -78°C and the temperature allowed to rise to 0°C , thereby trapping the dienal as it was formed. All four isomers of the undeca-1,3,5-triene have been described in the literature^{35,36} and the characteristic spectral feature of the 1,3*Z*,5*E*-isomer (**10b**) has been shown to be the ¹H n.m.r. signal of 5-H (δ 6.52, ddt, J 15, 10, *ca.* 1.5 Hz).³⁶ The synthetic sample of (**10b**) prepared in this study exhibited entirely consistent spectral data^{35,36} including the diagnostic n.m.r. signal for 5-H (δ 6.49, ddt, J 15, 11, 2 Hz).³⁶

In summary, we have shown that 2*Z*,4*E*-dienals and derivatives are readily available from the reaction between organometallic reagents and pyrylium perchlorate. The method is both general and stereoselective, and yields are fair to excellent. Application to a simple natural product has been demonstrated. The extension of the methodology to more complex systems is in progress.

Experimental

M.p.s were recorded on a Kofler hot-stage apparatus and are uncorrected. B.p.s quoted are the observed oven temperatures on Kugelrohr distillation at the pressure stated.

Dinitrophenylhydrazone derivatives of the dienals were prepared by standard methods,³⁷ and recrystallised from glacial acetic acid. Spectroscopic and analytical properties of these derivatives were consistent with the assigned structures. The 4-substituted 4*H*-pyrans (**4**) were unstable, and consequently it was not possible to obtain satisfactory analyses, although spectral data were consistent with the structures assigned. I.r. spectra (ν_{max}) were recorded, using a Perkin-Elmer 297 grating spectrometer, as thin films between sodium chloride plates unless otherwise stated. U.v. spectra (λ_{max}) were recorded using a Pye-Unicam SP800A spectrophotometer, as solutions in EtOH (unless otherwise stated), in matched quartz 1 cm cells. ¹H n.m.r. spectra (δ_{H}) were recorded using JEOL PMX-60 (unless otherwise stated) Bruker AM-360, JEOL FX-400 and Bruker WH-400 instruments. ¹³C n.m.r. spectra (δ_{C}) were recorded using a JEOL FX-100 instrument at 25.05 MHz. Unless otherwise stated, samples for n.m.r. spectrometry were prepared as solutions in deuteriochloroform, containing tetramethylsilane as internal standard. Mass spectra (m/z) were recorded on Kratos MS25, MS30, and VG ZAB-1F instruments. Chromatography refers to preparative centrifugal chromatography, carried out on silica gel plates (Merck 7749) using a ChromatotronTM Model 7924T or column chromatography using silica gel (Merck 7734) at normal pressure. All reactions conducted at low temperature, or involving organometallic reagents, were carried out using flame-dried apparatus. Organolithium reagents were titrated³⁸ before use. Methyl-lithium (in ether), butyl-lithium (in hexane), *s*-butyl-lithium (in hexane), *t*-butyl-lithium (in hexane), phenyl-lithium (in cyclohexane-ether), benzylmagnesium bromide (in ether), allylmagnesium bromide (in ether), di-isobutylaluminium hydride (in heptane), and 70% aqueous perchloric acid were purchased from the Aldrich Chemical Company. Other organometallic reagents were prepared immediately before use. Ether refers to diethyl ether, and petroleum refers to the fraction of boiling range $40\text{--}60^\circ\text{C}$, which was redistilled before use. Ether, THF, and 1,2-dimethoxyethane were purified by distillation from sodium-benzophenone ketyl before use. Sodium glutacetaldehyde dihydrate was prepared using the procedure of Becher.¹⁷

Pyrylium Perchlorate (1).—Pyrylium perchlorate was prepared using a modification of the procedure of Klages and Träger.¹³ Thus a solution of perchloric acid (aq. 70%; 75 ml) in ether (150 ml) was added in one portion to a suspension of sodium glutacetaldehyde dihydrate (10.0 g, 0.064 mol) in methanol (70 ml) at -20°C . The mixture clarified, then became turbid again, and was filtered to remove NaClO₄ after *ca.* 5 min. The filtrate was diluted with ether (150 ml), stored overnight at 4°C , and filtered to give pyrylium perchlorate (**1**) (4.1 g, 35%). Generally, the product isolated was analytically pure, and therefore suitable for organometallic reactions. Where purification was necessary, this was achieved by dissolution of the salt in 70% aqueous perchloric acid followed by precipitation with THF, giving pyrylium perchlorate as a white solid which was analysed prior to use (Found: C, 33.3; H, 2.7. Calc. for C₅H₅ClO₅: C, 33.3; H, 2.8%; δ_{H} (CF₃CO₂H) 8.40–8.60 (2 H, m), 9.20–9.50 (1 H, m), and 9.60–9.70 (2 H, m).

General Procedure for Addition of Organolithium Reagents to Pyrylium Perchlorate (1); Data for the Dienals (3a–g, i, j).—Pyrylium perchlorate (**1**) (0.20–1.26 g, 1.1–7.0 mmol) was suspended in THF (20 ml) [DME (5 ml) for entries vii and ix] under a nitrogen atmosphere at -78°C . The organolithium reagent (1.1 mol equiv.) was added over a short period of time,

and the resulting yellow or red solution was stirred for 15 min at the same temperature and then added to saturated aqueous ammonium chloride. The aqueous mixture was extracted twice with ether, and the combined extracts were washed once with water and once with brine and then dried (MgSO_4). Solvent was removed under reduced pressure, and the residue was purified by chromatography in dichloromethane-petroleum (1:1). The following 2*Z*,4*E*-dienals (**3**) were prepared by this procedure. In some reactions the corresponding *E,E*-isomers and the pyrans (**4**) were also formed—see Tables 1 and 2 for details.

(i) (2*Z*,4*E*)-5-Phenylpenta-2,4-dienal (**3a**) (96%; 2.4 mmol scale using phenyl-lithium) was obtained as a bright yellow oil (Found: M^+ , 158.0728. $\text{C}_{11}\text{H}_{10}\text{O}$ requires M^+ , 158.0732); ν_{max} . 3 040, 1 665, 1 620, 1 588, and 1 565 cm^{-1} ; δ_{H} 5.86 (1 H, dd, J 7.5 Hz, 10 Hz), 6.70–7.90 (8 H, m), and 10.18 (1 H, d, J 7.5 Hz); m/z 158 (M^+ , 87%), 129 ($M^+ - \text{CHO}$, 37), and 128 (74). Dinitrophenylhydrazone: m.p. 203–205 °C (lit.,²⁴ m.p. of *E,E*-isomer, 194–196 °C).

(ii) (2*Z*,4*E*)-*Nona*-2,4-dienal (**3b**) (81%; 7.0 mmol scale using butyl-lithium) was obtained as a very pale yellow liquid, b.p. ca. 75 °C/0.5 mmHg (Found: C, 77.9; H, 10.4. $\text{C}_9\text{H}_{14}\text{O}$ requires C, 78.2; H, 10.2%); λ_{max} . 280 nm (log ϵ 4.31); ν_{max} . 3 040, 2 770, 1 670, 1 640, and 1 575 cm^{-1} ; δ_{H} (360 MHz) 0.92 (3 H, t, J 7 Hz), 1.10–1.70 (4 H, m), 2.24 (2 H, dt, J 7 Hz, 7 Hz), 5.78 (1 H, dd, J 10.7 Hz, 8 Hz), 6.18 (1 H, dt, J 14.4 Hz, 7 Hz), 6.93 (1 H, dd, J 11.3 Hz, 10.7 Hz), 7.00 (1 H, dd, J 14.4 Hz, 11.3 Hz), and 10.17 (1 H, d, J 8 Hz); δ_{C} 13.86, 22.31, 30.76, 32.76, 124.29, 125.70, 147.07, 147.90, and 190.16; m/z 138 (M^+ , 11%), and 81 ($\text{C}_5\text{H}_5\text{O}^+$, 100). Dinitrophenylhydrazone: m.p. 147–148 °C (lit.,⁷ m.p. 147–148.5 °C; lit.,²³ m.p. of *E,E*-isomer, 138.5–141 °C).

(iii) (2*Z*,4*E*)-6-Methylocta-2,4-dienal (**3c**) (56%; 2.3 mmol scale using *s*-butyl-lithium) was obtained as a pale yellow, extremely air-sensitive oil; ν_{max} . 2 960, 2 920, 2 880, 1 665, and 1 640 cm^{-1} ; δ_{H} 0.90 (3 H, t, J 7.5 Hz), 1.07 (3 H, d, J 6.5 Hz), 1.35 (2 H, dq, J 2 Hz, 7.5 Hz), 1.90–2.60 (1 H, m), 5.60–6.40 (2 H, m), 6.5–7.1 (2 H, m), and 10.18 (1 H, d, J 7.5 Hz). Dinitrophenylhydrazone: m.p. 148–148.5 °C (lit.,²⁵ m.p. of *E,E*-isomer, 133–134.5 °C) (Found: C, 56.5; H, 5.7; N, 17.4. $\text{C}_{15}\text{H}_{18}\text{N}_4\text{O}_4$ requires C, 56.6; H, 5.7; N, 17.6%).

(iv) (2*Z*,4*E*)-6,6-Dimethylhepta-2,4-dienal (**3d**) (78%; 2.5 mmol scale using *t*-butyl-lithium) was obtained as a pale yellow oil, with a strong odour reminiscent of menthol (Found: M^+ , 138.1006. $\text{C}_9\text{H}_{14}\text{O}$ requires M^+ , 138.1045); ν_{max} . 2 980, 1 680, and 1 635 cm^{-1} ; δ_{H} 1.12 (9 H, s), 5.60–7.30 (4 H, m), and 10.18 (1 H, d, J 8 Hz); m/z 138 (M^+ , 6%), 137 (38), 95 (26), 94 (39), and 81 ($\text{C}_5\text{H}_5\text{O}^+$, 100). Dinitrophenylhydrazone: m.p. 150.5–152 °C (Found: C, 56.5; H, 5.8; N, 17.4. $\text{C}_{15}\text{H}_{18}\text{N}_4\text{O}_4$ requires C, 56.6; H, 5.7; N, 17.6%).

(v) (2*Z*,4*E*)-Hexa-2,4-dienal (**3e**)³⁹ (89%; 1.1 mmol scale using methyl-lithium) was obtained as a very pale yellow, malodorous liquid, b.p. ca. 180 °C/760 mmHg (Found: C, 74.3; H, 8.50; M^+ , 96.0557. $\text{C}_6\text{H}_8\text{O}$ requires C, 75.0; H, 8.4%; M^+ , 96.0575); ν_{max} . 3 040, 2 960, 1 670, 1 640, and 1 580 cm^{-1} ; δ_{H} 1.92 (3 H, d, J 6.5 Hz), 5.60–7.30 (4 H, m), and 10.17 (1 H, d, J 7.5 Hz); m/z 96 (M^+ , 34%), 81 ($\text{C}_5\text{H}_5\text{O}^+$, 100), 67 ($M - \text{CHO}$, 31) and 53 ($M^+ - \text{CH}_2\text{CHO}$, 33). Dinitrophenylhydrazone: m.p. 161–163 °C (lit.,⁷ m.p. 163–165 °C; lit.,²³ m.p. of *E,E*-isomer, 194.5–195.5 °C).

(vi) (2*Z*,4*E*,7)-Octa-2,4,7-trienal (**3f**) [30%; 2.1 mmol scale using allyl-lithium²¹] was obtained as a pale yellow, inseparable oily mixture (81:19) with 4-allyl-4*H*-pyran (**4f**) (Found: M^+ , 122.0729. $\text{C}_8\text{H}_{10}\text{O}$ requires M^+ , 122.0732); ν_{max} . 3 090, 3 050, 3 010, 2 990, 2 860, 1 670, 1 645sh, 1 635, and 1 578 cm^{-1} ; δ_{H} 2.15 (2 H from allyl pyran, t, J 6.5 Hz), 2.99 (2 H from octatrienal, t, J 6.5 Hz) [ratio of peaks 19:81], 4.60–5.30 (m), 5.50–6.40 (m), 6.70–7.30 (m) [ratio approx. 4:5:3], 10.22 (1 H from octatrienal, d, J 7.5 Hz); δ_{C} (**3f**) 36.93, 116.89, 125.00, 126.28, 134.45, 143.66, 147.36, and 190.28; m/z 122 (M^+ , 1%),

121 ($M^+ - \text{H}$, 1), 91 ($M^+ - \text{CHO}$, 17), and 81 ($\text{C}_5\text{H}_5\text{O}^+$, 100). Dinitrophenylhydrazone: m.p. 147–147.5 °C. After 2 weeks at –20 °C, n.m.r. analysis indicated the absence of the pyran (**4f**) and the presence of a mixture (ca. 1:1) of (2*Z*,4*E*,7)-Octa-2,4,7-trienal (**3f**) and (2*E*,4*E*,7)-octa(2,4,7-trienal (δ 9.55, br d, J 7 Hz, *CHO*).

(vii) (2*Z*,4*E*,6*E*)-Undeca-2,4,6-trienal (**3g**) [64%; 3.9 mmol scale using lithium butyldi-isobutylhex-1-enylaluminum, prepared⁴⁰ from hex-1-yne (0.35 g, 3.9 mmol) and di-isobutylaluminium hydride (1*M*; 4.3 ml, 3.7 mmol) in heptane (2 ml) at 50 °C followed by the addition of ether (3 ml) and BuLi (1.4*M*; 3 ml, 4.2 mmol) at room temperature] was obtained as a pale yellow oil (Found: C, 80.1; H, 10.1. $\text{C}_{11}\text{H}_{16}\text{O}$ requires C, 80.4; H, 9.8%); λ_{max} . 320 nm (log ϵ 4.43); ν_{max} . 3 040, 2 780, 2 740, 1 670, 1 640, 1 610, and 1 560 cm^{-1} ; δ_{H} 0.90 (3 H, br t, J 5.5 Hz), 1.10–1.60 (4 H, m), 2.20 (2 H, br dt, J ca. 6 Hz, ca. 5 Hz), 5.40–7.30 (6 H, m), and 10.10 (1 H, d, J 7.5 Hz); δ_{C} 13.86, 22.19, 31.00, 32.70, 123.58, 125.99, 129.63, 142.20, 143.19, 147.36, and 189.87; m/z 164 (M^+ , 25%) and 81 ($\text{C}_5\text{H}_5\text{O}^+$, 100).

(viii) (2*Z*,4*E*)-Undeca-2,4-dien-6-ynal (**3i**) [86%; 2.2 mmol scale using hex-1-ynyl-lithium in THF (1*M*; 1.9 ml, 1.9 mmol) generated from hex-1-yne (1.23 g, 15 mmol) and butyl-lithium (1.5*M*; 10 ml, 15 mmol) in THF (5 ml) at –70 °C] was obtained as a pale yellow oil (Found: C, 81.1; H, 8.8. $\text{C}_{11}\text{H}_{14}\text{O}$ requires C, 81.4; H, 8.7%); λ_{max} . 308 nm (log ϵ 4.56); ν_{max} . 3 050, 3 000, 2 770, 2 740, 2 210, 1 675, and 1 610 cm^{-1} ; δ_{H} 0.92 (3 H, br t, J 5.5 Hz), 1.10–1.70 (4 H, m), 2.20–2.60 (2 H, m), 5.96 (1 H, dt, J 14.5 Hz, 2.5 Hz), 6.82 (1 H, dd, J 7 Hz, 10 Hz), 6.87 (1 H, dd, J 10 Hz, 12 Hz), 7.42 (1 H, dd, J 12 Hz, 14.5 Hz), and 10.10 (1 H, d, J 7.5 Hz); δ_{C} 13.62, 19.55, 22.02, 30.59, 79.49, 99.81, 122.53, 127.64, 133.27, 145.78, and 189.75; m/z 162 (M^+ , 40%), 119 (38), 105 (76), and 91 (100).

(ix) (2*Z*,4*E*)-7-Phenylhepta-2,4-dien-6-ynal (**3j**) [65%; 4.4 mmol scale using lithium phenylacetylide, generated from phenylacetylene (0.50 g, 4.9 mmol) and butyl-lithium (1.5*M*; 3.3 ml, 4.9 mmol) in ether (7 ml)] was obtained as a yellow oil (Found: C, 85.9; H, 5.3. $\text{C}_{13}\text{H}_{16}\text{O}$ requires C, 85.7; H, 5.5%); λ_{max} . 330 nm (log ϵ 4.58); ν_{max} . 3 060, 2 740, 2 200, 1 670, 1 610, and 1 570 cm^{-1} ; δ_{H} 5.84 (1 H, dd, J 10 Hz, 8 Hz), 6.12 (1 H, d, J 14.5 Hz), 6.84 (1 H, dd, J 10 Hz, 14.5 Hz), 7.10–7.60 (6 H, m), and 10.14 (1 H, d, J 8 Hz); δ_{C} 88.42, 97.40, 121.12, 122.70, 128.16, 128.46 (2C), 128.98, 131.75 (2C), 134.56, 144.48, and 189.22; m/z 182 (M^+ , 81%), 181 ($M^+ - \text{H}$, 88), 153 ($M^+ - \text{CHO}$, 100), 152 (85), and 105 ($\text{C}_7\text{H}_5\text{O}^+$, 50).

(x) (2*Z*,4*E*)-5-(2-Thienyl)penta-2,4-dienal (**3l**) [48%; 1.6 mmol scale using 2-thienyl-lithium, prepared⁴¹ from thiophene (136 mg, 1.6 mmol) and butyl-lithium (1.38*M*; 1.17 ml, 1.6 mmol) in THF (5 ml)] was obtained as a pale yellow solid, which was recrystallised from petroleum to give very pale yellow needles, m.p. 49.8–50.4 °C (Found: C, 65.7; H, 4.9; S, 19.6. $\text{C}_9\text{H}_8\text{OS}$ requires C, 65.8; H, 4.9; S, 19.5%); ν_{max} . (Nujol) 3 080, 1 670, 1 655, and 1 610 cm^{-1} ; δ_{H} 5.82 (1 H, dd, J 7.5 Hz, 11.5 Hz), 6.60–7.80 (6 H, m), and 10.15 (1 H, d, J 7.5 Hz); m/z 164 (M^+ , 73%), 135 ($M^+ - \text{CHO}$, 100), and 91 (57). Dinitrophenylhydrazone: m.p. 207 °C.

Addition of Benzyl-lithium to Pyrylium Perchlorate (1): Preparation of (2Z,4E)-6-Phenylhexa-2,4-dienal (3h) and 4-Benzyl-4H-pyran (4h).—A solution of benzyl-lithium, generated from butyl-lithium (1.4*M*; 1.8 ml, 2.5 mmol) and toluene (5 ml) containing TMEDA (0.6 ml) at 0 °C, was added to a suspension of pyrylium perchlorate (**1**) (0.40 g, 2.2 mmol) in freshly distilled, dried 1,2-dimethoxyethane (5 ml) in a nitrogen atmosphere at –78 °C. The resulting red solution was stirred for 30 min at the same temperature, and then added to saturated aqueous ammonium chloride (50 ml). The mixture was extracted with petroleum (2 × 100 ml), and the combined extracts were washed with water and brine, dried over (MgSO_4) and

evaporated under reduced pressure to leave a yellow oil which was purified by chromatography in dichloromethane-petroleum (1:2) to give: (i) 4-benzyl-4*H*-pyran (**4h**) (156 mg, 41%) as a colourless oil which darkened rapidly with time; ν_{\max} . 3 095, 3 070, 3 040, 1 685, 1 625, and 1 605 cm^{-1} ; δ_{H} 2.74 (2 H, d, J 7 Hz), 2.80–3.20 (1 H, m), 4.65 (2 H, ddd, J 6.5 Hz, 3 Hz, 1.5 Hz), 6.23 (2 H, ddd, J 6.5 Hz, 1.5 Hz, 1.5 Hz), and 6.90–7.40 (5 H, m); δ_{C} 31.35, 46.14, 105.15 (2C), 126.17, 128.34 (2C), 129.34, (2C), 138.85, and 140.37; (2C) m/z 170 ($M^+ - 2\text{H}$, 12%), 129 (28), 115 (31), 91 (C_7H_7^+ , 50), and 81 ($\text{C}_5\text{H}_5\text{O}^+$, 100); and: (ii) (2*Z*,4*E*)-6-phenylhexa-2,4-dienal (**3h**) (102 mg, 27%) as a pale yellow oil (Found: M^+ , 172.0879. $\text{C}_{12}\text{H}_{12}\text{O}$ requires M^+ , 172.0888); λ_{\max} . 279 nm ($\log \epsilon$ 4.34); ν_{\max} . 3 090, 3 060, 3 040, 2 780, 2 740, 1 670, 1 635, 1 600, and 1 575 cm^{-1} ; δ_{H} 3.52 (2 H, d, J 7.2 Hz), 5.60–6.70 (2 H, m), 6.60–7.70 (7 H, m), and 10.10 (1 H, d, J 8 Hz); m/z 172 (M^+ , 8%), 143 ($M^+ - \text{CHHO}$, 8), 128 (17), 115 (10), 104 (19), 91 (16), and 81 ($\text{C}_5\text{H}_5\text{O}^+$, 100). Dinitrophenylhydrazone: m.p. 158.5–160 °C.

*Addition of 2-Lithio-1,3-dithiane to Pyrylium Perchlorate (1): Preparation of (2*Z*,4*E*)-5-(1,3-Dithian-2-yl)penta-2,4-dienal (3k) and 4-(1,3-Dithian-2-yl)-4*H*-pyran (4k).*—2-Lithio-1,3-dithiane, generated by treatment of a solution of 1,3-dithiane (0.25 g, 2.1 mmol) in freshly distilled, dried THF (5 ml) with butyl-lithium (2.5M; 0.84 ml, 2.1 mmol) at 0 °C, and stirring at that temperature for 1 h, was added under nitrogen to a suspension of pyrylium perchlorate (**1**) (0.32 g, 1.8 mmol) in freshly distilled, dried THF (15 ml) at –78 °C. The resulting red solution was stirred for 30 min at the same temperature and then added to saturated aqueous ammonium chloride (50 ml). The aqueous mixture was extracted with ether (2 × 50 ml) and the combined extracts were washed with water and brine, dried (MgSO_4), and evaporated under reduced pressure to leave a yellow oil which was separated by chromatography in dichloromethane-petroleum (1:1) to give: (i) 4-(1,3-dithian-2-yl)-4*H*-pyran (**4k**) (30 mg, 9%) as a colourless oil which darkened rapidly with time [Found: ($M^+ - 2$), 198.0188. $\text{C}_9\text{H}_{12}\text{OS}_2$ requires ($M^+ - 2$), 198.0174]; ν_{\max} . 3 075, 2 940, 2 900, 2 835, and 1 625 cm^{-1} ; δ_{H} 2.03 (2 H, septuplet, J 5 Hz), 2.89 (4 H, t, J 5 Hz), 3.10–3.40 (1 H, m), 4.00 (1 H, d, J 4.5 Hz), 4.70–5.00 (2 H, m), and 6.42 (2 H, br d, J 6 Hz); m/z 200 (M^+ , 1%), 198 ($M^+ - 2\text{H}$, 5), 119 (100), 94 (24), and 81 (74); and: (ii) (2*Z*,4*E*)-5-(1,3-dithian-2-yl)penta-2,4-dienal (**3k**) (170 mg, 49%) as a pale yellow oil (Found: M^+ , 200.0334. $\text{C}_9\text{H}_{12}\text{OS}_2$ requires M^+ , 200.0330); ν_{\max} . 3 050, 2 940, 2 910, 1 670, and 1 635 cm^{-1} ; δ_{H} 2.06 (2 H, septet, J 5 Hz), 2.91 (4 H, t, J 5 Hz), 4.73 (1 H, d, J 7 Hz), 5.89 (1 H, dd, J 9.5 Hz, 7 Hz), 6.18 (1 H, dd, J 14.5 Hz, J 7 Hz), 6.90 (1 H, dd, J 11 Hz, 9.5 Hz), 7.36 (1 H, dd, J 14.5 Hz, 11 Hz), and 10.09 (1 H, d, J 7 Hz); δ_{C} 24.95, 29.47 (2C), 46.32, 126.35, 128.40, 139.97, 145.31, and 189.92; m/z 200 (M^+ , 23%), 171 ($M^+ - \text{CHO}$, 10), 132 (31), 119 (54), 106 (29), and 97 (100). Dinitrophenylhydrazone: m.p. 195–195.5 °C.

General Procedure for Addition of Other Organometallic Reagents to Pyrylium Perchlorate (1): Pyrans (4a) and (4b).—The Grignard, organocuprate, $\text{Ph}_4\text{Ti}^{42}$ or $\text{Ph}_4\text{Zr}^{43}$ reagent (1.1 equiv.) in THF (ether in the case of allylmagnesium bromide) was added under nitrogen to a suspension of pyrylium perchlorate (**1a**) (0.20–0.44 g, 1.1–2.4 mmol) in freshly distilled, dried THF (15 ml) in a nitrogen atmosphere at –78 °C. The resulting yellow or red solution was stirred for 30 min at the same temperature and then added to saturated aqueous ammonium chloride. The aqueous mixture was extracted twice with ether, and the combined extracts were washed with water and brine, dried (MgSO_4), and evaporated under reduced pressure to leave a yellow oil which was purified by chromatography in dichloromethane-petroleum. The results of these reactions are summarised in Tables 1 and 2. In

addition to the compounds described earlier, the following were isolated: (i) 4-phenyl-4*H*-pyran (**4a**) (63%) [from the reaction of pyrylium perchlorate (**1**) with lithium diphenylcuprate, generated from phenyl-lithium and copper(I) iodide] as a colourless oil which darkened rapidly with time; ν_{\max} . 3 045 and 3 030 cm^{-1} ; δ_{H} 3.90–4.10 (1 H, m), 4.70–4.90 (2 H, m), 6.20–6.40 (2 H, m), and 7.10–7.50 (5 H, m); and (ii) 4-butyl-4*H*-pyran (**4b**) (41%) [from the reaction of pyrylium perchlorate (**1**) with lithium dibutylcuprate, generated from butyl-lithium and copper(I) bromide-dimethyl sulphide complex] as a colourless oil, which darkened rapidly with time; ν_{\max} . 2 965 and 2 935, cm^{-1} ; δ_{H} 0.91 (3 H, br t, J 5.5 Hz), 1.00–1.60 (6 H, m), 3.90–4.20 (1 H, m), 4.67 (2 H, ddd, J 5 Hz, 3 Hz, 1.5 Hz), and 6.27 (2 H, ddd, J 5 Hz, 1.5 Hz, 1.5 Hz); m/z 123 ($M^+ - \text{CH}_3$, 66%), 110 ($M^+ - \text{C}_2\text{H}_4$, 58), 109 ($M^+ - \text{C}_2\text{H}_5$, 35), 81 ($\text{C}_5\text{H}_5\text{O}^+$, 79), and 41 (100).

(2*Z*,4*E*)-Nona-2,4-dienoic Acid (**7**).—A solution of sodium chlorite (0.5 g) and potassium dihydrogen phosphate (0.5 g) in water (5 ml) was added to a stirred solution of (2*Z*,4*E*)-nonadienal (**3b**) (70 mg, 0.5 mmol) in *t*-butyl alcohol (12.5 ml) containing 2-methylbut-2-ene (3 ml), and the resulting mixture was stirred vigorously for 16 h at room temperature. Volatile material was removed under reduced pressure vacuum, and the residue was extracted twice with ether. The combined ethereal extracts were washed with water, dried (MgSO_4), and evaporated under reduced pressure to afford a pale yellow oil. Purification of the product by chromatography in dichloromethane-methanol (99:1) gave (2*Z*,4*E*)-nona-2,4-dienoic acid (**7**) (70 mg, 91%) as a pale yellow oil (Found: C, 70.0; H, 9.2. $\text{C}_9\text{H}_{14}\text{O}_2$ requires C, 70.1; H, 9.15%); ν_{\max} . 3 400–2 500, 1 690, 1 635, and 1 600 cm^{-1} ; δ_{H} 0.91 (3 H, br t, J 5.5 Hz), 1.20–1.60 (4 H, m), 2.21 (2 H, br q, J 7 Hz), 5.54 (1 H, d, J 11 Hz), 6.10 (1 H, dt, J 15 Hz, 7 Hz), 6.63 (1 H, dd, J 11 Hz, 11 Hz), 7.34 (1 H, dd, J 15 Hz, 11 Hz), and 10.58 (1 H, br s, OH); δ_{C} 13.86, 22.31, 30.88, 32.76, 114.60, 126.99, 147.185, 147.72, and 172.14; m/z 154 (M^+ , 21%), 109 ($M^+ - \text{CO}_2\text{H}$, 11), and 97 (100).

(2*Z*,4*E*)-Methyl Nona-2,4-dienoate (**8**).—Manganese dioxide (1.59 g) and sodium cyanide (0.23 g) were added to a stirred solution of the (2*Z*,4*E*)-nonadienal (**3b**) (130 mg, 0.94 mmol) in methanol (25 ml) containing glacial acetic acid (0.08 ml). The resulting suspension was stirred for 15 h, after which no starting material remained (t.l.c.). The mixture was filtered, the filtrate was evaporated under reduced pressure, and the residue was redissolved in water (20 ml). This aqueous solution was extracted with ether (2 × 25 ml), and the combined extracts were washed with water and brine, dried (MgSO_4), and evaporated under reduced pressure. Chromatography of the oily residue in dichloromethane-petroleum (1:3) gave (2*Z*,4*E*)-methyl nona-2,4-dienoate (155 mg, 98%) as a pale yellow oil (Found: C, 71.7; H, 9.7. $\text{C}_{10}\text{H}_{16}\text{O}$ requires C, 71.4; H, 9.6%); ν_{\max} . 3 060, 2 965, 2 940, 2 870, 1 725, 1 645, and 1 605 cm^{-1} ; δ_{H} 0.90 (3 H, br t, J 6 Hz), 1.05–1.60 (4 H, m), 2.00–2.40 (2 H, m), 3.70 (3 H, s), 5.54 (1 H, d, J 11 Hz), 6.03 (1 H, dt, J 15 Hz, 7 Hz), 6.53 (1 H, dd, J 11 Hz, 11 Hz), and 7.37 (1 H, br dd, J 15 Hz, 11 Hz); δ_{C} 13.91, 22.37, 31.00, 32.76, 50.96, 115.01, 126.93, 145.60, 145.78, and 166.85; m/z 168 (M^+ , 20%), 137 ($M^+ - \text{OMe}$, 12), and 111 ($M^+ - \text{CO}_2\text{Me}$, 100).

General Procedure for the Preparation of the Z,E-Dienols (9).—The organolithium reagent (1.0 mol equiv.) was added under nitrogen at –78 °C to a stirred suspension of pyrylium perchlorate (**1**) (0.25–1.00 g, 1.4–5.6 mmol) in freshly distilled, dried THF (20.25 ml) (for entries i, ii, and iv), or DME (10 ml) (for entries iii and v and vi). The mixture was stirred for 15 min at this temperature, after which HMPA (1 ml, probably not essential—see text) was added. The mixture was stirred for a

further 15 min at -78°C and then allowed to warm to 0°C during 30 min. After the mixture had been allowed to recool to -78°C , a second organolithium reagent or di-isobutylaluminium hydride (1.1 mol equiv.) was added to it. It was then stirred for a further hour at -78°C and then diluted with water. The aqueous mixture was extracted twice with ether, and the combined extracts were washed with water and brine, dried (MgSO_4), and evaporated under reduced pressure. Chromatography of the residue in dichloromethane-petroleum (2:1) gave the desired dienol. The following *Z,E*-dienols were prepared using this procedure.

(i) (6*Z*,8*E*)-Deca-6,8-dien-5-ol (**9a**) (57%; 1.4 mmol scale using methyl-lithium, followed by butyl-lithium) was obtained as a colourless oil; ν_{max} 3 400 and 3 020 cm^{-1} ; δ_{H} 0.88 (3 H, br t, J 5.5 Hz), 1.00–1.70 (6 H, m), 1.76 (3 H, d, J 5 Hz), 1.76 (1 H, br s, OH), 4.30–4.70 (1 H, m), 5.20 (1 H, dd, J 9.5 Hz, 9.5 Hz), and 5.40–6.60 (3 H, m); δ_{C} 14.06, 18.35, 22.71, 27.59, 37.30, 68.01, 126.77, 130.42, and 131.71 (2C); m/z 154 (M^+ , 12%), 153 ($M^+ - \text{H}$, 13), 125 (46), 97 (47), 43 (98), and 41 (100).

(ii) (5*Z*,7*E*)-3-Methylnona-5,7-dien-4-ol (**9b**) (60%; 2.0 mmol scale using methyl-lithium, followed by *s*-butyl-lithium) was obtained as a colourless oil (Found: C, 77.8; H, 11.7. $\text{C}_{10}\text{H}_{18}\text{O}$ requires C, 77.9; H, 11.8%); ν_{max} 3 420 and 3 025 cm^{-1} ; δ_{H} 0.70–1.10 (6 H, m), 1.10–1.80 (3 H, m), 1.80 (3 H, d, J 6.5 Hz), 2.20 (1 H, br s, OH), 4.32 (1 H, dd, J 5 Hz, 9.6 Hz), 5.24 (1 H, dd, J 9.6 Hz, 9.6 Hz), and 5.40–6.60 (3 H, m); m/z 154 (M^+ , 4%) and 97 (100).

(iii) (3*Z*,5*E*)-7-Methylnona-3,5-dien-2-ol (**9c**) (48%; 1.4 mmol scale using *s*-butyl-lithium, followed by methyl-lithium) was obtained as a colourless oil (Found: C, 77.8; H, 11.8. $\text{C}_{10}\text{H}_{18}\text{O}$ requires C, 77.9; H, 11.8%); ν_{max} 3 350 and 3 020 cm^{-1} ; δ_{H} 0.94 (3 H, t, J 7 Hz), 1.00 (3 H, d, J 6 Hz), 1.30 (3 H, d, J 6 Hz), 1.10–1.50 (2 H, m), 1.92 (1 H, br s, OH), 2.00–2.20 (1 H, m), 4.75 (1 H, m), 5.28 (1 H, dd, J 9.6 Hz, J 9.6 Hz), and 5.30–6.50 (3 H, m); m/z 154 (M^+ , 1%), 97 (18), 96 (24), 91 (20), and 43 (100).

(iv) (3*Z*,5*E*)-7,7-Dimethylocta-3,5-dien-2-ol (**9d**) (52%; 1.6 mmol scale using *t*-butyl-lithium, followed by methyl-lithium) was obtained as a colourless oil, b.p. (Kugelrohr) $75^{\circ}\text{C}/0.8$ mmHg (lit.,⁴⁴ b.p. $106^{\circ}\text{C}/16$ mmHg); ν_{max} 3 350, 3 020, 2 960, 2 930, and 2 870 cm^{-1} ; δ_{H} 1.01 (9 H, s; lit.,⁹ δ 1.02), 1.27 (3 H, d, J 6 Hz), 1.56 (1 H, br s, OH), 4.26 (1 H, br d, J 6 Hz), and 4.60–6.50 (4 H, m).

(v) (2*Z*,4*E*)-1,5-Diphenylpenta-2,4-dien-1-ol (**9e**) (49%; 1.7 mmol scale using 2 mol equiv. of phenyl-lithium) was obtained as a yellow oil; λ_{max} 290 nm (log ϵ 4.48); ν_{max} 3 400, 3 070, and 3 040 cm^{-1} ; δ_{H} 2.60 (1 H, br s, OH), 5.30–6.50 (4 H, m), 6.75 (1 H, d, J 19 Hz), and 7.10–7.50 (10 H, m); δ_{C} 69.98, 123.35, 125.88 (2C), 126.58 (2C), 127.46, 127.87, 128.52 (4C), 130.04, 133.09, 134.92, 136.91, and 143.08; m/z 236 (M^+ , 4%), 218 ($M^+ - \text{H}_2\text{O}$, 6), 158 (16), and 105 (100).

(vi) (2*Z*,4*E*)-Deca-2,4-dien-1-ol (**9f**) [60%; 5.6 mmol scale using pentyl-lithium (0.83M; 6.65 ml, 5.5 mmol) prepared from bromopentane (15 mmol) and lithium (70 mmol) in ether (15 ml), followed by di-isobutylaluminium hydride] was obtained as a colourless oil; ν_{max} 3 350 and 3 030 cm^{-1} ; δ_{H} (400 MHz), 0.88 (3 H, t, J 7 Hz), 1.20–1.40 (7 H, m), 2.09 (2 H, tdd, J 8 Hz, 7.1 Hz, 1.4 Hz), and 4.26–4.32 (2 H, m; at 60 and 100 MHz, this appears as a doublet, δ 4.29, J 7 Hz; lit.,⁶ δ 4.32, d, J 7 Hz), 5.48 (1 H, dt, J 10 Hz, 7 Hz), 5.75 (1 H, dtd, J 15 Hz, 7.1 Hz, 0.5 Hz), 6.06 (1 H, dtd, J 11 Hz, 10 Hz, 1.2 Hz, 0.5 Hz), and 6.29 (1 H, dtd, J 15 Hz, 11 Hz, 1.4 Hz, 1 Hz); δ_{C} 14.03, 22.60, 29.00, 31.53, 32.88, 58.48, 125.05, 127.58, 130.63, and 136.97.

(1,3*Z*,5*E*)-Dodeca-1,3,5-trien-7-yne (**10a**).—Hexynyl-lithium in ether [1M (see **3i**); 2.0 ml, 2.0 mmol] was added dropwise to a stirred solution of pyrylium perchlorate (**1**) (0.30 g, 1.7 mmol) in 1,2-dimethoxyethane (5 ml) at -78°C . After being stirred at the same temperature for 10 min, the mixture was allowed to

warm to room temperature over a further 30 min after which it was again cooled to -78°C . A solution of methylene-triphenylphosphorane, prepared from methyltriphenylphosphonium bromide (0.75 g, 2.0 mmol) and butyl-lithium (1.5M; 1.3 ml, 1.95 mmol) in THF (8 ml) was added in one portion, following which the mixture was stirred at -78°C for 1 h, and then added to water. The aqueous mixture was extracted twice with petroleum and the combined extracts were washed with water and brine, dried (MgSO_4), and removed under reduced pressure. Chromatography of the residue in petroleum gave (1,3*Z*,5*E*)-dodeca-1,3,5-trien-7-yne (**10a**) (85 mg, 33%) as a pale yellow oil (Found: C, 90.2; H, 10.1. $\text{C}_{12}\text{H}_{16}$ requires C, 89.9; H, 10.1%); λ_{max} 278 (log ϵ 4.64), 290 (4.79), and 303 nm (4.75); ν_{max} 3 095, 3 040, 3 020, and 2 210 cm^{-1} ; δ_{H} 0.90 (3 H, br t, J 5.5 Hz), 1.10–1.80 (4 H, m), 2.10–2.50 (2 H, m), 5.00–7.30 (7 H, m); δ_{C} 13.56, 19.37, 21.96, 30.82, 80.02, 94.41, 113.02, 118.89, 129.05, 130.98, 131.86, and 135.33; m/z 160 (M^+ , 67%), 117 (96), 115 (58), and 91 (C_7H_7^+ , 100).

(1,3*Z*,5*E*)-Undeca-1,3,5-triene (**10b**).—Pentyl-lithium [0.79M; 2.78 ml, 2.2 mmol; generated from 1-bromopentane (0.1 mol) and lithium (0.2 mol) in pentane (50 ml) under argon] was added dropwise to a stirred solution of pyrylium perchlorate (**1**) (0.39 g, 2.2 mmol) in THF (5 ml) at -78°C . After the mixture had been stirred at the same temperature for 30 min, a solution of methylenetriphenylphosphorane, prepared from methyltriphenylphosphonium bromide (1.00 g, 2.8 mmol) and butyl-lithium (2.5M solution; 1.0 ml, 2.5 mmol) in THF (5 ml) was added to it in one portion at -78°C ; following which it was allowed to warm to 0°C over 30 min; it was then diluted with water. The aqueous mixture was extracted twice with petroleum, and the combined extracts were washed with water and brine, dried (MgSO_4), and evaporated under reduced pressure. Chromatography of the residue in petroleum gave (1,3*Z*,5*E*)-undeca-1,3,5-triene (**10b**) (281 mg, 87%) as a pale yellow oil; λ_{max} (hexane) 273 (log ϵ 4.45), 264 (4.51), and 252 (4.45); ν_{max} 3 090, 3 035, 2 960, 2 930, 2 860, 1 800, 1 640, 1 620, 1 465, 1 440, 975, 945, and 900 cm^{-1} ; δ_{H} (400 MHz), 0.90 (3 H, t, J 7.5 Hz), 1.20–1.40 (6 H, m), 2.10–2.15 (2 H, m), 5.09 (1 H, br d), 5.19 (1 H, dd, J 16.9 Hz, 1.8 Hz), 5.74 (1 H, dt, J 15.0 Hz, 7.2 Hz), 5.85–6.00 (2 H, m), 6.49 (1 H, dtd, J 15.0 Hz, 11.0 Hz, 2.0 Hz) [lit.,³⁶ δ 6.52, dtd, J 15.0 Hz, 10.0 Hz, ca. 1.5 Hz], and 6.80 (1 H, dt, J 16.9 Hz, 10.6 Hz); δ_{C} 14.03, 22.54, 29.00, 31.47, 32.94, 117.01, 125.52, 127.69, 130.34, 132.27, and 136.80; m/z 150 (M^+ , 19%), 111 (28), 109 (27), 97 (44), 95 (46), 81 (55), 80 (57), 69 (69), 57 (83), and 55 (100). The spectral data were consistent with published^{35,36} values.

Acknowledgements

We are grateful to the S.E.R.C. for a C.A.S.E. studentship (M. F.) and a postdoctoral research assistantship (J. M. H.) and to the Royal Society of Chemistry for the award of a Hickinbottom Fellowship (R. J. K. T.). We also thank Dr. S. C. Burford for his interest and advice, Fisons Pharmaceutical Division for generous financial support, Professor J. E. Baldwin for helpful mechanistic suggestions (summarised in Scheme 2) and the S.E.R.C. WH-400 n.m.r. service for highfield spectra.

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Received 22nd June 1988; Paper 8/02484G