

Ring Opening of 2*H*-Pyrans Promoted by Organometallic Reagents. Synthesis of Dienic Alcohols

Angel Alberola,* Celia Andrés, Alfonso González Ortega, Rafael Pedrosa, and Martina Vicente
 Departamento de Química Orgánica, Universidad de Valladolid, Doctor Mergelina s/n, 47011-Valladolid,
 Spain

2*H*-Pyrans react with organoaluminiums, Grignard reagents, and lithium derivatives to afford, with good yield, conjugated dienols resulting from 1,2-addition processes of the organometallic reagent to the dienones in equilibrium with the 2*H*-pyrans. Those organometallic reagents act on sterically hindered 2*H*-pyrans to give dienols and unsaturated ketones (1,4- and 1,6-addition products) as by-products.

In a previous work we have described the behaviour of 2*H*-1-benzopyrans towards organoaluminium and organomagnesium derivatives as leading to *o*-allylphenols stereoselectively; the control of experimental conditions allowed us to prepare both *Z*- and *E*-isomers.^{1,2}

We report now the synthesis of dienic alcohols (3)–(6), (11), and (12), and γ,δ - (7), β,γ - (8)–(10), and α,β -unsaturated ketones (13), (14) by reaction of 2*H*-pyrans (1) — in equilibrium with their isomeric dienones³ (2) with organometallic compounds as shown in Scheme 1.

The reactions of 2*H*-pyrans with organometallic derivatives lead to 1-hydroxy-2,4-dienes and unsaturated ketones with yields depending on the structure of the substrate, the nature of the organometallic reagent, and experimental conditions (Table).

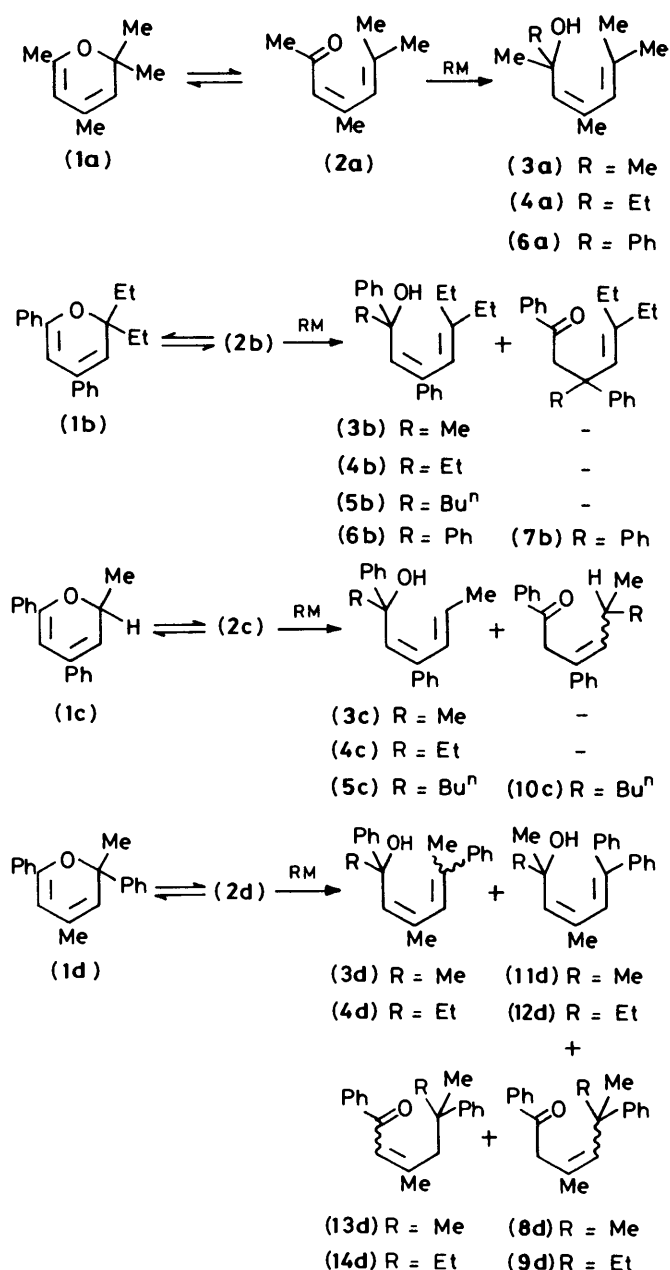
It is noteworthy that the reaction of 2,4-dimethyl-2,6-diphenyl-2*H*-pyran (1d) with trimethyl aluminium is nearly quantitative (entry 27), and, in general, the 1,2-addition processes are of high yield. In contrast, phenylmagnesium bromide reacts with 2,2-diethyl-4,6-diphenyl-2*H*-pyran (1b) to give a mixture of ketone (7b) and the corresponding hydroxy diene (6b) (entry 20), while only the hydroxy derivative (6a) is formed by reaction with 2,2,4,6-tetramethyl-2*H*-pyran (1a) (entry 7).

The reactions of 2*H*-pyrans with organocuprates are not of synthetic interest, since the processes lead to polymeric mixtures of unidentified products, except in the reaction of 2-methyl-4,6-diphenyl-2*H*-pyran (1c) with lithium di-*n*-butylcuprate which yields the ketone (10c) as an equimolar mixture of geometrical isomers (entry 26). On the other hand, the starting 2*H*-pyran (1b) is recovered unchanged after 24 h at reflux with the organocuprate generated from ethylmagnesium bromide and copper(i) chloride (entry 14).

In general, 2*H*-pyrans behave in a similar fashion towards trialkylaluminium, organomagnesium, an organolithium derivatives; only a small quantitative difference was observed when *n*-butyl derivatives were used (compare entries 15, 16, and 18), and the steric requirements of the alkyl group attached to aluminium influence the final yield only in the reactions of 2-methyl-4,6-diphenyl-2*H*-pyran (1c).

In contrast with the case of benzopyrans,¹ u.v. irradiation of the reaction mixtures does not modify the stereochemistry of the dienols, but slows the rate of the process, increasing the reaction time and giving a mixture of by-products.

It was necessary to know the configuration of the double bonds in the final products to establish the correlation between the stereochemistry and the reaction pathway. The geometry of the 1,2-double bond was determined by the electrocyclic ring opening of the 2*H*-pyran system, and the *E* configuration of the second one in compounds (3c), (4c), and (5c) was established on



RM = R MgX, RLi, R₃Al, R₂CuLi

Scheme 1.

Table. Reaction of 2*H*-pyrans with organometallic compounds

Entry	Pyran	Organometallic reagent	Solvent	Temp. (°C)	<i>t</i> (h)	Products (%) ^a
1	(1a)	Me ₃ Al	PhH	25	2	(3a) (70)
2	(1a)	MeMgI	Et ₂ O	25	2	(3a) (75)
3	(1a)	MeLi	Et ₂ O	25	1	(3a) (75)
4	(1a)	Me ₂ CuLi	Et ₂ O	-10	40	<i>b</i>
5	(1a)	Et ₃ Al	PhH	25	4	(4a) (73)
6	(1a)	EtLi	Et ₂ O	25	6	(4a) (73)
7	(1a)	PhMgBr	Et ₂ O	25	4	(6a) (55) ^c
8	(1b)	Me ₃ Al	PhH	25	4	(3b) (83)
9	(1b)	MeMgI	Et ₂ O	25	48	(3b) (80)
10	(1b)	MeLi	Et ₂ O	25	24	(3b) (80)
11	(1b)	Et ₃ Al	PhH	25	24	(4b) (80)
12	(1b)	Et ₃ Al	Et ₂ O	40	24	(4b) (50)
13	(1b)	EtMgBr	Et ₂ O	40	6	(4b) (60)
14	(1b)	EtMgBr + Cu ₂ Cl ₂	Et ₂ O	40	24	(1b) (100)
15	(1b)	Bu ₃ Al	PhH	25	2	(5b) (80)
16	(1b)	BuMgBr	Et ₂ O	40	10	(5b) (52)
17	(1b)	BuMgBr	Et ₂ O	40	5	(5b) (48) ^d
18	(1b)	BuLi	n-C ₆ H ₁₄	25	4	(5b) (59)
19	(1b)	Bu ₂ CuLi	Et ₂ O	25	16	<i>b</i>
20	(1b)	PhMgBr	Et ₂ O	40	6	(6b) (30), (7b) (35)
21	(1c)	Me ₃ Al	PhH	25	0.5	(3c) (93)
22	(1c)	Et ₃ Al	PhH	25	2.5	(4c) (60)
23	(1c)	EtMgBr	Et ₂ O	40	6	(4c) (44)
24	(1c)	EtMgBr	Et ₂ O	40 ^d	2	<i>e</i>
25	(1c)	Bu ₃ Al	PhH	25	12	(5c) (55)
26	(1c)	Bu ₂ CuLi	Et ₂ O	-10	24	(10c) (32) ^f
27	(1d)	Me ₃ Al	PhH	25	2.5	(3d) (98) ^g
28	(1d)	MeMgI	Et ₂ O	25	4	(3d) (30), ^h (11d) (54)
29	(1d)	MeLi	Et ₂ O	25	2	(3d) (69), ^h (13d) (26)
30	(1d)	MeLi	Et ₂ O	40 ^d	5	(3d) (20), (13d) (5), (8d) (35)
31	(1d)	Et ₃ Al	PhH	25	2	(4d) (18), (12d) (50)
32	(1d)	Et ₃ Al	Et ₂ O	25	5	<i>i</i>
33	(1d)	EtLi	Et ₂ O	25	5	(4d) (30), (9d) + (14d) (34)

^a Yields refer to isolated and purified compounds. ^b Polymeric mixture. ^c 12% of (1a) recovered. ^d Under u.v. irradiation. ^e Complex mixture of alcohols and ketones. ^f An equimolar mixture of *E*- and *Z*-isomers. ^g Isomeric mixture: 3*Z*,5*Z* (70%) and 3*Z*,5*Z* (30%). ^h Isomeric mixture: 3*Z*,5*E* (75%) and 3*Z*,5*Z* (25%). ⁱ Complex mixture of products.

the basis of the coupling constants of the olefinic protons, while the stereochemistry of both isomers of alcohol (3d) was correlated by their chemical shifts (chemical shifts for vinylic proton, *cis* to Ph, in *Z,E* isomer > chemical shifts for the same proton, *trans* to Ph, in *Z,Z* isomer).⁴ In this way, the stereochemistry of alcohol (4d) was tentatively assigned as (4*Z*,6*E*). The ¹H n.m.r. spectral data were also employed as discussed above to determine the identity of the geometrical isomers of β,γ-unsaturated ketones (10c) (molar ratio *E*:*Z* 1:1), and mechanistic considerations allow us to propose the *E* configuration for compound (8d). On the other hand, no isomerization of the 1,2-double bond on the dienone occurred since we always found the same stereochemistry for this bond in all the compounds isolated (3)—(6), (11), and (12).

Although no additional attempts to establish the reaction mechanism were made, the stereochemistry of the products could be rationalized on the basis of the thermodynamic stability of dienones (2) in equilibrium with 2*H*-pyrans (1). Consequently, products (3)—(6) and (7) will be formed by 1,2- or 1,4-addition processes respectively from the most stable dienone (2), generated from (1) (Scheme 2).

The configuration of β,γ-unsaturated ketones (8)—(10) resulting from a 1,6-addition process will also be determined by the steric requirements in the transition state (15). Although the most stable conformation is *s-trans*, the increase in the size of R⁴ determines the equilibrium proportions of other conformers leading to the formation of a mixture of geometrical isomers.

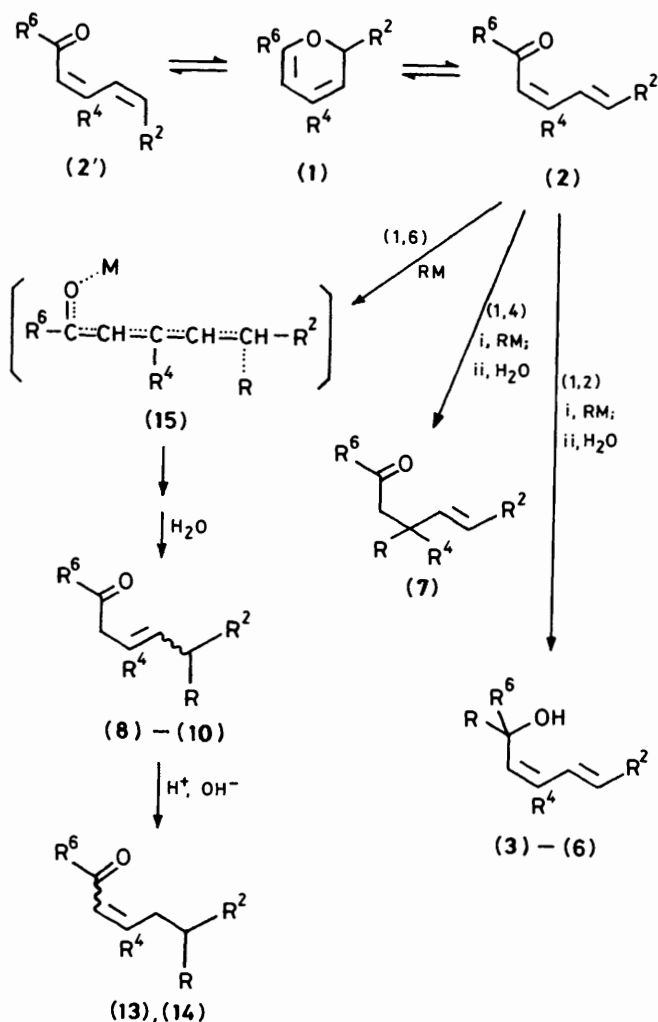
Finally, it is interesting to note that the pyran (1d) behaves towards organometallic reagents in a different way to that of its homologues; it reacts with methyl-lithium to give a mixture of 1,2-addition products and β,γ- and α,β-unsaturated ketones, and with aluminium and magnesium derivatives to yield mixtures of isomeric dienols (3d), (11d), (4d), and (12d), some of which [(11d) and (12d)] are formed by transposition of the phenyl group at C-2, probably before the main reaction commences; this rearrangement may be promoted by the organometallic reagent.

Experimental

M.p.s were determined with a Büchi capillary melting point apparatus and are uncorrected. I.r. spectra were recorded on a Pye-Unicam SP 1100 spectrometer. ¹H N.m.r. were recorded on a Varian T-60A instrument at 60 MHz with SiMe₄ as internal standard (δ 0). Mass spectra were determined on a Hewlett-Packard 5995 spectrometer.

Synthesis of 2H-Pyran.—2,2,4,6-Tetramethyl-2*H*-pyran (1a)⁵ and 2,4-dimethyl-2,6-diphenyl-2*H*-pyran (1d)⁶ were prepared by described methods.

2,2-Diethyl-4,6-diphenyl-2*H*-pyran (1b). By Gompper and Christmann's method,⁷ to a stirred solution of ethylmagnesium bromide (0.48 mol) in ether (350 ml) at 0 °C was added a solution of 4,6-diphenylpyran-2-one⁸ (40 g, 0.16 mol) in the



Scheme 2. Superscripts to R denote the position of the substituents on the pyran ring

same solvent. The reaction mixture was allowed to rise to room temperature and was kept overnight before being hydrolysed by addition of a mixture of ice (500 g) and hydrochloric acid. After being washed (water), and dried over anhydrous magnesium sulphate, the mixture was chromatographed on a column of silica gel with hexane as solvent, to afford compound (1b) (25 g, 53%) as a white solid, m.p. 70 °C; δ_{H} (CDCl₃) 0.9 (t, 6 H), 1.7 (q, 4 H), 5.3 (d, 1 H), 5.9 (d, 1 H), and 7.0–7.5 (m, 10 H); $\bar{\nu}_{\text{max}}$ (Nujol) 1 575 and 1 600 cm⁻¹ (Calc. for C₂₁H₂₂O: C, 86.85; H, 7.64. Found: C, 86.9; H, 7.6%).

2-Methyl-4,6-diphenyl-2H-pyran (1c). A mixture of 2-methyl-4,6-diphenyl-3,4-dihydropyran-4-ol⁹ (26.6 g, 0.1 mol), silica gel (80 g) (Merck, Art. 7734); activated at 120 °C for 3 h, and anhydrous toluene (250 ml) was heated at 110 °C for 1 h (the cyclization was monitored by t.l.c.). After the reaction had finished, the mixture was filtered without cooling and the silica gel was washed with hot toluene (4 × 75 ml). The combined filtrate and washings were evaporated under reduced pressure and the residue was purified by column chromatography (silica gel; hexane–benzene 2:1). The title product (1c) (8.2 g, 33%) was isolated as an unstable oil (95% pure by ¹H n.m.r.), which was used in the next step without further purification; δ_{H} (CCl₄) 1.6 (d, 3 H), 5.0 (m, 1 H), 5.5 (d, 1 H), 6.2 (s, 1 H), and 7.1–7.8 (m, 10 H); $\bar{\nu}_{\text{max}}$ (film) 1 570 and 1 650 cm⁻¹.

Reaction of 2H-Pyrans with Organometallic Reagents. General method.—To a solution of organometallic reagent

(30 mmol) in the appropriate solvent (50 ml) was slowly added dropwise a solution of the 2H-pyran in the appropriate solvent (40 ml) (see Table for experimental conditions). The mixture was stirred until reaction had ceased (t.l.c.) and was hydrolysed with ice–water. The mixture was filtered, and the aqueous phase was extracted with ether (4 × 50 ml); the organic phase was washed with water and dried over anhydrous magnesium sulphate. The solvent was evaporated off under reduced pressure and the residue was chromatographed on a column of silica gel (30 g of Kieselgel-60 per gram of mixture) with hexane–benzene (10:3) as solvent. The purification process must be as fast as possible because the dienols can be decomposed or isomerized by the silica gel.

The obtained dienols could not be crystallized, distilled, or derivatized (as urethanes, benzoates, or sulphonates) because they decomposed very quickly. Their identities have been established by i.r., ¹H n.m.r., mass spectroscopy, and analytical data.

(3Z)-2,4,6-Trimethylhepta-3,5-dien-2-ol (3a).¹⁰ δ_{H} (CCl₄) 1.3 (s, 6 H), 1.8 (m, 9 H), 5.3 (q, 1 H), and 5.9 (s, 1 H); $\bar{\nu}_{\text{max}}$ (film) 1 650 and 3 450 cm⁻¹; *m/z* 154 (M⁺, 1.1%), 139 (100), 136 (2.1), and 43 (68.6) (Calc. for C₁₀H₁₈O: C, 77.87; H, 11.76. Found: C, 77.65; H, 11.9%).

(3E)-6-Ethyl-2,4-diphenylocta-3,5-dien-2-ol (3b). Oil, δ_{H} (CCl₄) 0.7 (t, 3 H), 0.9 (t, 3 H), 1.6 (s, 3 H), 2.0 (m, 4 H), 5.8 (s, 1 H), 6.3 (d, 1 H), and 7.0–7.5 (m, 10 H); $\bar{\nu}_{\text{max}}$ (film) 1 640 and 3 450 cm⁻¹; *m/z* 306 (M⁺, 2.8%), 288 (13.6), 105 (100), and 91 (31.7) (C₂₂H₂₆O requires C, 86.23; H, 8.55. Found: C, 86.9; H, 8.7%).

(3E,5E)-2,4-Diphenylhepta-3,5-dien-2-ol (3c). Light yellow oil, δ_{H} (CCl₄) 1.5 (d, 3 H), 1.6 (s, 3 H), 5.4 (m, 1 H), 5.8 (s, 1 H), 6.7 (d, 1 H), and 7.0–7.5 (m, 10 H); $\bar{\nu}_{\text{max}}$ (film) 970, 1 640, and 3 450 cm⁻¹ (C₁₉H₂₀O requires C, 86.32; H, 7.63. Found: C, 86.2; H, 7.7%).

(3Z,5Z)-4-Methyl-2,6-diphenylhepta-3,5-dien-2-ol (3Z,5Z)- (3d). Yellow oil, δ_{H} (CCl₄) 1.6 (s, 3 H), 1.9 (m, 6 H), 5.8 (q, 1 H), 6.1 (s, 1 H), and 7.2–7.6 (m, 10 H); $\bar{\nu}_{\text{max}}$ (film) 1 640 and 3 450 cm⁻¹; *m/z* 278 (M⁺, 0.9%), 260 (13.6), 105 (100), and 91 (33.0) (C₂₀H₂₂O requires C, 86.29; H, 7.97. Found: C, 86.1; H, 8.0%).

(3Z,5E)-4-Methyl-2,6-diphenylhepta-3,5-dien-2-ol (3Z,5E)- (3d). Yellow oil δ_{H} (CCl₄) 1.6 (s, 3 H), 1.9 (m, 6 H), 5.9 (q, 1 H), 6.3 (s, 1 H), and 7.2–7.6 (m, 10 H); $\bar{\nu}_{\text{max}}$ (film) 1 640 and 3 450 cm⁻¹; *m/z* 278 (M⁺, 2.0%), 260 (19.0), 105 (100), and 91 (12.0) (Found: C, 86.2; H, 8.1%).

(4Z)-3,5,7-Trimethylocta-4,6-dien-3-ol (4a). Yellow oil, δ_{H} (CCl₄) 0.9 (t, 3 H), 1.2 (s, 3 H), 1.4 (q, 2 H), 1.7–1.9 (m, 9 H), 5.3 (m, 1 H), and 6.0 (s, 1 H); $\bar{\nu}_{\text{max}}$ (film) 1 660 and 3 450 cm⁻¹; *m/z* 168 (M⁺, 2.6%), 150 (5.4), 69 (85.7), and 43 (100) (C₁₁H₂₀O requires C, 78.85; H, 11.98. Found: C, 78.6; H, 12.1%).

(4E)-7-Ethyl-3,5-diphenylnona-4,6-dien-3-ol (4b). Oil, δ_{H} (CCl₄) 0.7 (t, 3 H), 0.8 (t, 3 H), 0.9 (t, 3 H), 1.5–2.1 (m, 6 H), 5.8 (s, 1 H), 6.3 (d, 1 H), and 7.0–7.4 (m, 10 H); $\bar{\nu}_{\text{max}}$ (film) 1 640 and 3 450 cm⁻¹; *m/z* 320 (M⁺, 2.2%), 302 (2.2), 105 (87.1), and 91 (100) (C₂₃H₂₈O requires C, 86.20; H, 8.81. Found: C, 86.1; H, 8.7%).

(4E,6E)-3,5-Diphenylocta-4,6-dien-3-ol (4c). Yellow oil, δ_{H} (CCl₄) 0.9 (t, 3 H), 1.7 (d, 3 H), 1.9 (q, 2 H), 5.4 (m, 1 H), 5.8 (s, 1 H), 6.9 (d, 1 H), and 7.1–7.6 (m, 10 H); $\bar{\nu}_{\text{max}}$ (film) 970, 1 650, and 3 450 cm⁻¹; *m/z* 278 (M⁺, 1.4%), 260 (16.3), 105 (100), and 91 (58.0) (C₂₀H₂₂O requires C, 86.29; H, 7.97. Found: C, 86.1; H, 7.8%).

(4Z,6E)-5-Methyl-3,7-diphenylocta-4,6-dien-3-ol (4d). Yellow oil, δ_{H} (CCl₄) 0.9 (t, 3 H), 1.7 (d, 3 H), 1.8 (q, 2 H), 1.9 (d, 3 H), 5.9 (s, 1 H), 6.3 (s, 1 H), and 7.0–7.4 (m, 10 H); $\bar{\nu}_{\text{max}}$ (film) 3 450 cm⁻¹ (C₂₁H₂₄O requires C, 86.26; H, 8.27. Found: C, 86.2; H, 8.35%).

(6E)-9-Ethyl-5,7-diphenylundeca-6,8-dien-5-ol (5b). Yellow oil, δ_{H} (CDCl₃) 0.7 (t, 3 H), 0.9 (t, 6 H), 1.3 (m, 4 H), 1.6–2.2

(m, 6 H), 6.0 (s, 1 H), 6.5 (d, 1 H), and 7.2–7.5 (m, 10 H); $\bar{\nu}_{\max}$ (film) 1 640 and 3 450 cm^{-1} ; m/z 348 (M^{+} , 0.8%), 330 (7.8), 105 (41.0), and 91 (100) ($\text{C}_{25}\text{H}_{32}\text{O}$ requires C, 86.16; H, 9.25. Found: C, 86.3; H, 9.2%).

(6E,8E)-5,7-Diphenyldeca-6,8-dien-5-ol (**5c**). Yellow oil, δ_{H} (CDCl_3) 0.8 (t, 3 H), 1.4 (m, 4 H), 1.6 (d, 3 H), 1.9 (m, 2 H), 5.4 (m, 1 H), 5.9 (s, 1 H), 6.8 (d, J 16 Hz, 1 H), and 7.1–7.7 (m, 10 H); $\bar{\nu}_{\max}$ (film) 970, 1 650, and 3 450 cm^{-1} ; m/z 306 (M^{+} , 2.4%), 288 (9.1), 105 (93.3), and 91 (100) ($\text{C}_{22}\text{H}_{26}\text{O}$ requires C, 86.23; H, 8.55. Found: C, 86.2; H, 8.6%).

(3Z)-4,6-Dimethyl-2-phenylhepta-3,5-dien-2-ol (**6a**). Yellow oil, δ_{H} (CCl_4) 1.5 (s, 3 H), 1.9 (d, 9 H), 5.6 (m, 1 H), 5.8 (m, 1 H), and 7.0–7.5 (m, 5 H); $\bar{\nu}_{\max}$ (film) 1 610 and 3 500 cm^{-1} ($\text{C}_{15}\text{H}_{20}\text{O}$ requires C, 83.29; H, 9.32. Found: C, 83.2; H, 9.3%).

(2E)-5-Ethyl-1,1,3-triphenylhepta-2,4-dien-1-ol (**6b**). Yellow oil, δ_{H} (CCl_4) 0.6 (t, 3 H), 0.9 (t, 3 H), 1.7 (q, 2 H), 1.9 (q, 2 H), 6.0 (m, 1 H), 6.6 (d, 1 H), and 7.0–7.5 (m, 15 H); $\bar{\nu}_{\max}$ (film) 1 650 and 3 450 cm^{-1} ($\text{C}_{27}\text{H}_{28}\text{O}$ requires C, 88.0; H, 7.66. Found: C, 88.1; H, 7.8%).

5-Ethyl-1,3,3-triphenylhept-4-en-1-one (**7b**). δ_{H} (CCl_4) 0.5 (t, 3 H), 1.0 (t, 3 H), 1.5 (q, 2 H), 2.0 (q, 2 H), 3.9 (s, 2 H), 6.2 (s, 1 H), and 7.0–7.5 (m, 15 H); $\bar{\nu}_{\max}$ (film) 1 710 cm^{-1} . 2,4-Dinitrophenylhydrazones, yellow solid, m.p. 148–149 °C (from ethanol) ($\text{C}_{33}\text{H}_{32}\text{N}_4\text{O}_4$ requires C, 72.24; H, 5.88; N, 10.21. Found: C, 72.4; H, 6.0; N, 10.1%).

(E)-3,5-Dimethyl-1,5-diphenylhex-3-en-1-one (**E**)-(8d). White solid, m.p. 63–65 °C (from hexane–benzene); δ_{H} (CCl_4) 1.2 (s, 6 H), 1.8 (s, 3 H), 3.8 (s, 2 H), 5.7 (s, 1 H), and 7.2–8.2 (m, 10 H); $\bar{\nu}_{\max}$ (Nujol) 1 700 cm^{-1} ($\text{C}_{20}\text{H}_{22}\text{O}$ requires C, 86.29; H, 7.97. Found: C, 86.4; H, 8.1%).

3,5-Dimethyl-1,5-diphenylhept-3-en-1-one (**9d**). White solid, m.p. 67–69 °C (from hexane–benzene); δ_{H} (CCl_4) 1.0 (t, 3 H), 1.5 (s, 3 H), 1.7 (m, 2 H), 2.2 (d, 3 H), 3.7 (s, 2 H), 5.8 (m, 1 H), and 7.2–8.1 (m, 10 H); $\bar{\nu}_{\max}$ (Nujol) 1 700 cm^{-1} ($\text{C}_{21}\text{H}_{24}\text{O}$ requires C, 86.26; H, 8.27. Found: C, 86.4; H, 8.1%).

(E)-5-Methyl-1,3-diphenylnon-3-en-1-one (**E**)-(10c). Yellow oil, δ_{H} (CCl_4) 1.0–2.6 (m, 12 H), 2.3 (m, 1 H), 4.1 (s, 2 H), 5.8 (d, 1 H), and 7.2–8.2 (m, 10 H); $\bar{\nu}_{\max}$ (film) 1 690 cm^{-1} ($\text{C}_{22}\text{H}_{26}\text{O}$ requires C, 86.23; H, 8.55. Found: C, 86.3; H, 8.4%).

(Z)-5-Methyl-1,3-diphenylnon-3-en-1-one (**Z**)-(10c). Yellow oil, δ_{H} (CCl_4) 1.0–2.6 (m, 12 H), 2.3 (m, 1 H), 3.9 (s, 2 H), 5.4 (d, 1 H), and 7.2–8.2 (m, 10 H); $\bar{\nu}_{\max}$ (film) 1 690 cm^{-1} (Found: C, 86.2; H, 8.4%).

2,4-Dimethyl-6,6-diphenylhexa-3,5-dien-2-ol (**11d**). Yellow oil, δ_{H} (CCl_4) 1.5 (s, 6 H), 2.1 (s, 3 H), 5.8 (s, 1 H), 6.1 (s, 1 H), and 7.0–7.4 (m, 10 H); $\bar{\nu}_{\max}$ (film) 1 640 and 3 450 cm^{-1} ; m/z 278 (M^{+} , 0.2%), 260 (19.8), 105 (100), and 91 (20.1) ($\text{C}_{20}\text{H}_{22}\text{O}$ requires C, 86.29; H, 7.97. Found: C, 86.2; H, 8.1%).

3,5-Dimethyl-7,7-diphenylhepta-4,6-dien-3-ol (**12d**). Oil, δ_{H} (CCl_4) 0.9 (t, 3 H), 1.6 (s, 3 H), 1.9 (q, 2 H), 2.0 (d, 3 H), 5.8 (m, 1 H), 6.1 (s, 1 H), and 7.0–7.4 (m, 10 H); $\bar{\nu}_{\max}$ (film) 1 640 and 3 450 cm^{-1} ($\text{C}_{21}\text{H}_{24}\text{O}$ requires 86.26; H, 8.27. Found: C, 86.1; H, 8.4%).

3,5-Dimethyl-1,5-diphenylhex-2-en-1-one (**13d**). White crystals, m.p. 74–75 °C (from hexane–benzene); δ_{H} (CCl_4) 1.3 (s, 6 H), 2.1 (d, 3 H), 3.2 (s, 2 H), 5.8 (m, 1 H), and 7.2–8.0 (m, 10 H); $\bar{\nu}_{\max}$ (film) 1 690 cm^{-1} ($\text{C}_{20}\text{H}_{22}\text{O}$ requires C, 86.29; H, 7.97. Found: C, 86.1; H, 7.8%).

3,5-Dimethyl-1,5-diphenylhept-2-en-1-one (**14d**). White solid, m.p. 70–72 °C (from hexane–benzene); δ_{H} (CCl_4) 1.0 (t, 3 H), 1.4 (s, 3 H), 1.7 (m, 2 H), 2.2 (d, 3 H), 3.2 (s, 2 H), 5.8 (m, 1 H), and 7.2–8.2 (m, 10 H); $\bar{\nu}_{\max}$ (film) 1 690 cm^{-1} ($\text{C}_{21}\text{H}_{24}\text{O}$ requires C, 86.26; H, 8.27. Found: C, 86.1; H, 8.2%).

References

- 1 A. Alberola, A. González Ortega, R. Pedrosa, J. L. Pérez Bragado, and J. F. Rodríguez Amo, *J. Chem. Soc., Perkin Trans. I*, 1983, 1209; A. Alberola, A. González Ortega, R. Pedrosa, J. L. Pérez Bragado, and M. Vicente, *ibid.*, 1984, 1259.
- 2 A. Alberola, A. González Ortega, R. Pedrosa, and M. Vicente, *Synthesis*, 1984, 238.
- 3 T. A. Gosink, *J. Org. Chem.*, 1974, **39**, 1942 and references therein.
- 4 E. Pretsch, T. Clerc, J. Seibl, and W. Simon, 'Tabellen zur Strukturklärung Organischer Verbindungen mit Spektroskopischen Methoden,' Springer Verlag, Berlin, 1976.
- 5 A. Hinnen and J. Dreux, *Bull. Soc. Chim. Fr.*, 1964, 1492.
- 6 P. Rouillier, D. Gagnaire, and J. Dreux, *Bull. Soc. Chim. Fr.*, 1966, 689.
- 7 R. Gompper and O. Christmann, *Chem. Ber.*, 1961, **94**, 1784.
- 8 F. Arndt and B. Eistert, *Dtsch. Chem. Ges.*, 1925, **58**, 2318.
- 9 A. Duperrier, M. Moreau, S. Gelin, and J. Dreux, *Bull. Soc. Chim. Fr.*, 1974, 2207.
- 10 A. Duperrier and J. Dreux, *Tetrahedron Lett.*, 1970, 3127.

Received 16th June 1986; Paper 6/1209