the solvent gave 500 mg of **3c + 4c + 5c** as a yellow, viscous syrup, which was chromatographed on silica gel (Wakogel C-200). Elution with $CHCl_3$–MeOH–12 M $NH_4OH$ (150:10:1) gave pure samples of **3c** (150 mg), **4c** (80 mg), and **5c** (200 mg).

**3c:** NMR $\delta$ 1.28 (3 H, s, C-1 Me), 2.35 (3 H, s, N-Me), 3.83 (3 H, s, O-Me), 4.83 (1 H, d, $J$ = 5.0 Hz, C-7 H), 6.78 (1 H, d, $J$ = 3.0 Hz, C-11 H), 6.88 (1 H, double d, $J$ = 8.0, $J'$ = 3.0 Hz, C-9 H), 7.60 (1 H, d, $J$ = 8.0 Hz, C-8 H), 1.55–3.25 (10 H, m).

**4c:** bp 110–120 °C (0.01 mmHg) (bath temperature); ir (neat) 1670 $cm^{-1}$ (C=C); NMR $\delta$ 1.36 (3 H, s, C-1 Me), 2.36 (3 H, s, N-Me), 3.16 and 3.28 (2 H, AB, $J_{AB}$ = 10.0 Hz, C-5 $H_2$), 3.84 (3 H, s, O-Me), 6.27 (1 H, s, C-7 H), 6.73 (1 H, double d, $J$ = 8.5, $J'$ = 2.5 Hz, C-9 H), 6.88 (1 H, d, $J$ = 2.5 Hz, C-11 H), 7.17 (1 H, d, $J$ = 8.5 Hz, C-8 H), 1.45–2.70 (6 H, m); mass spectrum $m/e$ 243.1631 ($M^+$, calcd for $C_{16}H_{21}NO$, 243.1632).

**5c:** mp 73–75 °C (from hexane); ir (Nujol) 3350 $cm^{-1}$ (broad, OH); NMR $\delta$ 1.31 (3 H, s, C-1 Me), 2.21 (3 H, s, N-Me), 2.63 (1 H, s, exchangeable with $D_2O$, OH), 3.82 (3 H, s, O-Me), 4.26 (1 H, d, $J$ = 3.5 Hz, C-7 H), 6.76 (1 H, double d, $J$ = 8.0, $J'$ = 2.5 Hz, C-9 H), 6.82 (1 H, d, $J$ = 2.5 Hz, C-11 H), 7.24 (1 H, d, $J$ = 8.0 Hz, C-8 H), 1.45–3.20 (9 H, m). Anal. Calcd for $C_{16}H_{23}NO_2$: C, 73.53; H, 8.87; N, 5.36. Found: C, 73.26; H, 8.88; N, 5.30.

**II. Reaction of 3a. 3a** gave an 80% yield of **3a + 4a + 5a. 4a:** bp 105–110 °C (0.02 mmHg) (bath temperature); ir (neat) 1680 $cm^{-1}$ (C=C); NMR $\delta$ 2.36 (3 H, s, N-Me), 2.95 and 3.61 (2 H, AB, $J_{AB}$ = 10.0 Hz, C-5 $H_2$), 6.24 (1 H, s, C-7 H), 1.17–2.95 (7 H, m), 7.13 (4 H, m, aromatic H); mass spectrum $m/e$ 199.1370 ($M^+$, calcd for $C_{14}H_{17}N$, 199.1361).

**5a:** mp 108–109 °C (from hexane); ir (Nujol) 3270 $cm^{-1}$ (OH); NMR $\delta$ 2.20 (3 H, s, N-Me), 2.47 (1 H, s, exchangeable with $D_2O$, OH), 4.26 (1 H, d, $J$ = 2.2 Hz, C-7 H), 1.50–3.25 (10 H, m), 7.18 (4 H, m, aromatic H). Anal. Calcd for $C_{14}H_{19}NO$: C, 77.37; H, 8.81; N, 6.45. Found: C, 77.03; H, 8.64; N, 6.50.

**III. Reaction of 3b. 3b** gave a 70% yield of **3b + 4b + 5b. 4b:** bp 110–115 °C (0.02 mmHg) (bath temperature); ir (neat) 1680 $cm^{-1}$ (C=C); NMR $\delta$ 1.37 (3 H, s, C-1 Me), 2.34 (3 H, s, N-Me), 3.13 and 3.50 (2 H, AB, $J_{AB}$ = 10.0 Hz, C-5 $H_2$), 4.25 (1 H, s, C-7 H), 7.17 (4 H, m, aromatic H), 1.20–2.70 (6 H, m); mass spectrum $m/e$ 213.1525 ($M^+$, calcd for $C_{15}H_{19}N$, 213.1517).

**5b:** mp 103–104 °C (from hexane); ir (Nujol) 3250 $cm^{-1}$ (OH); NMR $\delta$ 1.34 (3 H, s, C-1 Me), 2.22 (3 H, s, N-Me), 4.28 (1 H, d, $J$ = 2.8 Hz, C-7 H), 7.27 (4 H, m, aromatic H), 1.20–3.30 (10 H, m). Anal. Calcd for $C_{15}H_{21}NO$: C, 77.88; H, 9.15; N, 6.06. Found: C, 77.68; H, 9.03; N, 6.28.

**IV. Reaction of 3d. 3d** gave a 75% yield of **4d. 4d:** bp 120–130 °C (0.01 mmHg) (bath temperature); ir (neat) 1670 $cm^{-1}$ (C=C); NMR $\delta$ 0.79 (3 H, d, $J$ = 7.0 Hz, C-12 Me), 1.31 (3 H, s, C-1 Me), 2.37 (3 H, s, N-Me), 3.05 and 3.45 (2 H, AB, $J_{AB}$ = 10.0 Hz, C-5 $H_2$), 3.80 (3 H, s, O-Me,), 6.16 (1 H, s, C-7 H), 6.63 (1 H, double d, $J$ = 8.0, $J'$ = 2.5 Hz, C-9 H), 6.78 (1 H, d, $J$ = 2.5 Hz, C-11 H), 7.06 (1 H, d, $J$ = 8.0 Hz, C-8 H), 1.50–2.73 (5 H, m); mass spectrum $m/e$ 257.1778 ($M^+$, calcd for $C_{17}H_{23}NO$, 257.1780).

**V. Reaction of 4a.** Reflux of **4a** with 1 N HCl for 3.5 h gave a 90% yield of **3a + 4a + 5a.**

**VI. Reaction of 4b.** Reflux of **4b** with 1 N HCl for 3 h gave an 85% yield of **3b + 4b + 5b.**

**VII. Reaction of 4d.** Reflux of **4d** with 1 N HCl for 3 h gave a 95% yield of recovery of **4d.**

**VIII. Reaction of 5a.** Reflux of **5a** for 3.5 h gave an 85% yield of **3a + 4a + 5a.**

**IX. Reaction of 5b.** Reflux of **5b** with 1 N HCl for 3 h gave a 90% yield of **3b + 4b + 5b.**

**X. Reaction of 6.** Reflux of **6** (211 mg) with 1 N HCl (20 ml) for 1 h gave a mixture of **6** and **7** (185 mg). The mixture was chromatographed on a silica gel column. Elution with $CHCl_3$–MeOH (150:10) gave pure samples of **6** and **7.** Compound **6** was identified by comparison of ir spectrum with that of the authentic sample.

**7:** colorless, viscous oil; ir (neat) 3340 $cm^{-1}$ (OH); NMR $\delta$ 1.27 (3 H, s, C-1 Me), 2.00 (3 H, s, N-Me), 3.75 (3 H, s, O-Me), 4.47 (1 H, s, C-6 H), 6.67 (1 H, double d, $J$ = 9.0, $J'$ = 2.5 Hz, C-8 H), 6.70 (1 H, d, $J$ = 2.5 Hz, C-10 H), 7.15 (1 H, d, $J$ = 9.0 Hz, C-7 H). Picrate: mp 197–203 °C (from MeOH). Anal. Calcd for $C_{15}H_{21}NO_2 \cdot C_6H_3N_3O_7$: C, 52.94; H, 5.08; N, 11.76. Found: C, 53.14; H, 5.06; N, 11.57.

**Reaction of 3c with HCl in MeOH.** A solution of **3c** (500 mg) and 12 M HCl (1 ml) in MeOH (10 ml) was refluxed for 2 h, the solvent, evaporated, diluted with $H_2O$, basified with 10% NaOH, and extracted with $CHCl_3$. After drying ($Na_2SO_4$), the solvent was evaporated to give 300 mg of **3'c + 4c + 5'c** (3:1:3). The mixture was chromatographed on silica gel (Wakogel C-200). Elution with $CHCl_3$–MeOH–12 M $NH_4OH$ (150:10:1) gave pure samples of **3'c** (110 mg), **4c** (30 mg, identified by comparison of ir spectrum with that of the authentic sample) and **5'c** (100 mg).

**3'c:** bp 150–160 °C (1.5 mmHg) (bath temperature); NMR $\delta$ 1.22 (3 H, s, C-1 Me), 2.24 (3 H, s, N-Me), 3.48 (3 H, s, C-7 O-Me), 3.76 (3 H, s, C-10 O-Me), 4.28 (1 H, d, $J$ = 4.0 Hz, C-7 H), 6.69 (1 H, double d, $J$ = 8.0, $J'$ = 2.8 Hz, C-9 H), 6.62 (1 H, d, $J$ = 2.8 Hz, C-11 H), 7.43 (1 H, d, $J$ = 8.0 Hz, C-8 H), 1.56–2.88 (9 H, m). Anal. Calcd for $C_{17}H_{25}NO_2$: C, 74.14; H, 9.15; N, 5.09. Found: C, 73.88; H, 8.91; N, 4.70.

**5'c:** bp 150–160 °C (1.5 mmHg) (bath temperature); NMR 1.28 (3 H, s, C-1 Me), 2.22 (3 H, s, N-Me), 3.33 (3 H, s, C-7 O-Me), 3.76 (3 H, s, C-10 O-Me), 3.68 (1 H, d, $J$ = 2.5 Hz, C-7 H), 6.64 (1 H, double d, $J$ = 8.0, $J'$ = 2.5 Hz, C-9 H), 6.72 (1 H, d, $J$ = 2.5 Hz, C-11 H), 7.07 (1 H, d, $J$ = 8.0 Hz, C-8 H). Anal. Calcd for $C_{17}H_{25}NO_2$: C, 74.14; H, 9.15; N, 5.09. Found: C, 74.29; H, 9.15; N, 5.09.

**Reaction of 3c with 1 N DCl.** A solution of **3c** (101 mg) in 1 N DCl (6 ml) was refluxed for 1 h. After cooling, the mixture was basified with 10% NaOH, extracted with $CHCl_3$, and dried ($K_2CO_3$). Evaporation of the solvent gave 99 mg of a yellow oil. The NMR showed that it was a mixture of olefin **4c,** 6-deuterio-7$\beta$-hydroxy **3''c,** and 6-deuterio-7$\alpha$-hydroxy compound **5''c** in the ratio 1:2:4 [C-7 proton signal of **4c,** $\delta$ 6.20 (singlet); C-7 proton signal of **3''c,** $\delta$ 4.78 (singlet); C-7 proton signal of **5''c,** $\delta$ 4.25 (singlet)].

**Reaction of 6 with 1 N DCl.** Reflux of **6** (90 mg) in 1 N DCl (6 ml) gave a mixture of **6** and **7** (70 mg). The NMR showed that substitution of C-5 hydrogen of **6** and **7** with deuterium did not occur at all.

**Registry No.—3'c,** 60363-78-2; **3''c,** 60363-79-3; **4c,** 60363-80-6; **5c,** 60409-21-4; **5'c,** 60409-20-3; **5''c,** 60384-71-6; **6,** 60363-81-7; **7,** 60384-72-7; **7** picrate, 60409-18-9; 4-methyl-4-(2-dimethylaminoethyl)-3,4-dihydronaphthalen-1(2*H*)-one, 60363-82-8; 4-methyl-4-(2-methylaminoethyl)-3,4-dihydronaphhalen-1(2*H*)-one HCl, 54782-00-2; 1,4-dimethyl-2,3,4,5-tetrahydro-1,6-methano-1*H*-4-benzazonin-7(6*H*)-one picrate, 60384-73-8; 1,4-dimethyl-2,3,4,5-tetrahydro-1,6-methano-1*H*-4-benzazonin-7(6*H*)-one, 54782-07-9; 1,4-dimethyl-2,3,4,5-tetrahydro-1,6-methano-1*H*-4-benzazonin-7(6*H*)-one HCl, 60384-74-9; 1,3-dimethyl-9-methoxy-1,2,3,4,5,6-hexahydro-1,5-methano-3-benzazocine, 37639-69-3; 1,3-dimethyl-9-methoxy-1,2,3,4-tetrahydro-1,5-methano-3-benzazocin-6(5*H*)-one, 60363-83-9.

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## (*E*)- and (*Z*)-4-Methyl-5-[5-(2,6,6-trimethylcyclohexen-1-yl)-3-methyl-2(*E*),4(*E*)-pentadienylidene]-2(5*H*)-furanone. Synthesis and Spectral Properties


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In the course of some other research on vitamin A and its derivatives, we became interested in the preparation of the

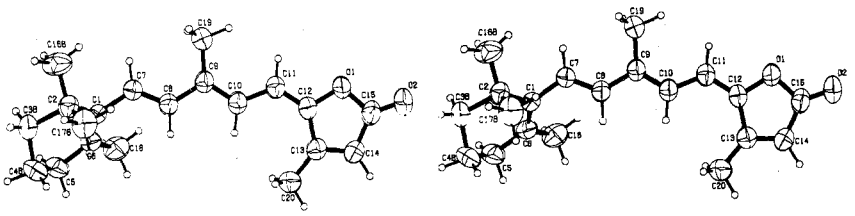
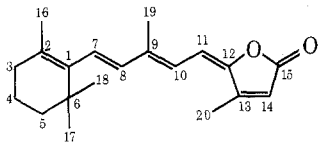
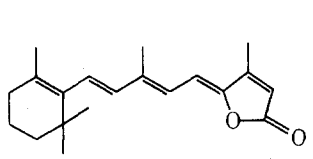


**Figure 1.** Stereodrawing of 1 showing one of the two conformers which are present in the crystal. Atoms C(3)B, C(4)B, C(16)B, and C(17)B are the half-weight carbon atoms of the "B" conformer. The thermal ellipsoids scaled to the 50% probability level and the hydrogen atoms are shown as spheres of an arbitrary size.

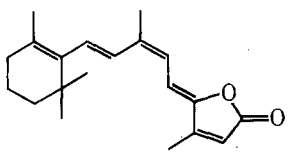
(*E*)- and (*Z*)-2(5*H*)furanones, **1** and **2**, respectively, related to retinoic acid.[1]



**1**

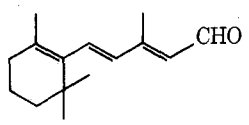


**2**

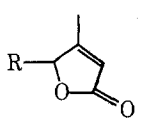


**3**

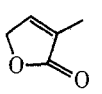
During the progress of this work, reports of the x-ray crystal structure determinations of **2** and its 9-cis isomer **3** appeared.[2,3] Although these papers stated that these compounds resulted from the reaction of *trans*-β-ionylideneacetaldehyde (**4**) and 3-methylbut-2-enolide (**5a**), no synthetic details could



**4**



**5**



**6**

| R |
|---|
| a H |
| b Br |
| c $^{+}PPh_3Br^{-}$ |

be found in the chemical literature. This paper reports the synthesis and spectral characterization including $^{13}C$ NMR of **1** and **2**, and the x-ray structure analysis of **1**, which was not previously reported.

The synthetic approach was analogous to the synthesis of freelingyne,[4,5] which utilized a Wittig reagent prepared from the isomeric butenolide **6**.[6]

The lactone **5a** and bromolactone **5b** were prepared as previously described.[7] The bromolactone **5b** was reacted immediately with triphenylphosphine to give the phosphonium bromide **5c**. Wittig reaction of **5c** and *all-trans*-β-ionylidineacetaldehyde[8] (**4**) in dimethylformamide with sodium hydride as base afforded a mixture of **1** and **2**. Chromatographic purification and crystallization afforded a less polar, higher melting compound. After being stored at −20 °C for 3 days, the mother liquors afforded a crystalline fraction consisting of two crystal forms which could be separated manually. One corresponded to the less polar compound; the second could be further purified by recrystallization from cold (−20 °C) pentane to give a more polar, lower melting isomer. Although the isomers displayed slightly different spectral properties, the unambiguous assignment of structure on this basis was not possible. Thus the structure of the crystalline less polar isomer **1** was determined by single-crystal x-ray diffraction analysis. The conformation of the molecule is shown in Figure 1. The C(6)–C(1)–C(7)–C(8) torsion angle is −53° (see Figure 1 for the atom labeling scheme).

**Table I. Crystal Data for 1 and 2**[a]

| | 1 | 2 | |
|---|---|---|---|
| | | Data from ref 2 | Measured crystal data |
| Space group | $P2_1/a$ | $P\bar{1}$ | $P\bar{1}$ |
| $a$ | 15.218 (2) Å | 6.87 (1) | 6.870 (2) |
| $b$ | 10.347 (3) Å | 7.51 (1) | 7.528 (6) |
| $c$ | 11.934 (2) Å | 18.67 (1) | 18.835 (8) |
| $\alpha$ | | 81.04 (12) | 80.37 (5) |
| $\beta$ | 108.60 (1)° | 83.77 (12) | 83.51 (3) |
| $\gamma$ | | 68.96 (12) | 69.05 (7) |
| $Z$ | 4 | 2 | 2 |
| $d_{calcd}$ | 1.115 g cm$^{-3}$ | 1.12 | |
| $\mu$ (Cu K$\alpha$) | 5.5 cm$^{-1}$ | | |

[a] The formula and formula weight for **1** and **2** are $C_{20}H_{26}O_2$ and 298.43.

The crystal data are given in Table I. The intensity data were measured on a Hilger-Watts diffractometer. The size of the crystal used for data collection was approximately 0.25 × 0.40 × 0.75 mm. No absorption correction was made. Of the 3621 accessible reflections with $\theta < 76°$, 3014 had intensities which were significantly greater than background. The structure was solved by a multiple solution procedure[9] and was refined by full-matrix least squares.

During the preliminary refinement it became apparent that the crystals were disordered. The disorder arises from a 1:1 mixture of the two possible puckered conformations of the cyclohexene ring. To account for the disorder the atoms C(3), C(4), C(16), and C(17) were each replaced by two atoms of half weight, corresponding to the two conformations of the cyclohexene ring.

The preliminary refinement was continued with anisotropic temperature factors for all atoms. A difference Fourier calculated at the end of this refinement had peaks at reasonable positions for all of the ordered hydrogens. The positions of all hydrogen atoms were calculated. Two sets of half-weighted hydrogen atoms were used for the carbons involved in the disorder and also for C(5). In the final refinement the hydrogen atoms were included in the structure factor calculations but their parameters were not refined. The final difference Fourier has no peaks or holes greater than ±0.2 e A$^{-3}$. The final discrepancy index is $R$ = 0.057 for the 3014 observed reflections.

The crystal data for the more polar isomer **2** were measured and compared with the previously published values (Table I). The unit cell given by Thackeray and Gafner[2] is related to the cell given in Table I by the transformation (0,0,1/0,−1,0/1,0,0). Intensity data were measured for the isomer **2**. There were 1560 observed reflections with $\theta < 57°$. Three cycles of full-matrix least squares, starting with the published atomic parameters, resulted in a discrepancy index of $R$ = 0.119 for the 1560 observed reflections (all atoms anisotropic,

Table II. $^{13}C$ NMR Spectral Data for 1 and 2[c]

| Carbon atom | Multiplicity[a] | δc 1 | δc 2 |
|---|---|---|---|
| 15 | s | 168.5 | 168.8 |
| 13 | s | 152.4 | 153.7 |
| 12 | s | 149.1 | 149.4 |
| 9 | s | 143.0 | 141.9 |
| 1 | s | 137.4 | 137.3 |
| 8 | d | 136.9 | 136.8 |
| 2 | s | 130.3 | 130.8 |
| 7 | d | 130.1 | 130.1 |
| 10 | d | 121.7 | 122.4 |
| 14 | d | 118.1 | 155.1 |
| 11 | d | 113.0 | 107.5 |
| 5 | t | 39.5 | 39.6 |
| 6 | s | 34.2 | 34.2 |
| 3 | t | 33.0 | 33.2 |
| 17, 18[b] | q | 28.9 | 28.9 |
| 16 | q | 21.7 | 21.7 |
| 4 | t | 19.1 | 19.2 |
| 20 | q | 15.7 | 12.8 |
| 19 | q | 12.3 | 11.6 |

[a] Single frequency off-resonance multiplicity. [b] Two-carbon peak. [c] See 1 for numbering of carbon atoms.

no hydrogens), thus conclusively confirming the structure of **2**.

The $^{13}C$ NMR spectral data for compounds **1** and **2** are given in Table II. The chemical shifts for these two compounds are very similar to those of *all-trans*-retinoic acid and its isomers,[10] and the majority of peaks can be readily assigned. However, there are three carbon atoms—carbon atoms 10, 11, and 12—which differ significantly in chemical shift from those of the retinoic acids and cannot be assigned by direct comparison. The unassigned carbon atoms due to C-10 and C-11 are found in the spectral region from ~107 to 123 ppm. In both **1** and **2**, the chemical shifts of C-11 would be expected at higher field than those of C-10, since C-11 is closer to the lactone ring. In addition, a larger chemical shift difference would also be expected for C-11 than for C-10 in going from **1** to **2**. The chemical shifts of C-10 and C-11 in *all-trans*-retinal occur at 129.4 and 132.4 ppm, respectively.[10] Thus, the peaks found for **1** and **2** at 113.0 and 107.5 ppm were assigned to C-11 (upfield shift of ~21 ppm; Δδ 5.5 ppm); the peaks at 121.7 and 122.4 ppm were assigned to C-10 (upfield shift of ~9 ppm; Δδ 0.7 ppm). Because it is directly bonded to oxygen, C-12 should exhibit a large downfield shift in both compounds when compared to the retinoic acids; the downfield shift should be approximately the same in both compounds. Thus, C-12 is assigned to the carbon atoms at 149.1 and 149.4 ppm for **1** and **2**, respectively.

## Experimental Section

Melting points were determined on a Kofler micro hot stage and are corrected values. The $^{13}C$ NMR spectra were recorded on 100 mg of each compound in deuteriochloroform solution on a Varian XL-100 NMR spectrometer at 25.2 MHz in the Fourier transform mode. The spectra were obtained using a 5000-Hz sweep width and an 8K data table. Elemental and spectral analyses and x-ray structure determinations were carried out by the Physical Chemistry Department, Hoffmann-La Roche Inc.

**(2,5-Dihydro-3-methyl-5-oxofuran-2-yl)triphenylphosphonium Bromide (5c).** A mixture of 13.28 g (0.135 mol) of the butenolide **5a**,[7] 26.4 g (0.149 mol) of *N*-bromosuccinimide, and 200 ml of carbon tetrachloride was heated to the reflux with a light source for 2 h. The mixture was allowed to cool and was filtered; the filtrate was concentrated in vacuo to give 23.3 g (0.131 mol) of crude 4-bromobutenolide **5b**. Without further purification, this was combined with 38 g (0.145 mol) of triphenylphosphine and 250 ml of benzene and heated to the reflux for 5 h. The mixture was allowed to cool to room temperature overnight and then was filtered to give 41.4 g (0.094 mol) of phosphonium salt **5c**. This material was used in the next step without further purification.

**(*E*)-4-Methyl-5-[5-(2,6,6-trimethylcyclohexen-1-yl)-3-methyl-2(*E*),4(*E*)-pentadienylidene]-2(5*H*)-furanone (1).** To a cooled (5 °C) suspension of 17.2 g (78.2 mmol) of $C_{15}$ aldehyde **4**, 41.4 g (94 mmol) of phosphonium salt **5c**, and 150 ml of dry dimethylformamide, 2.26 g (94 mmol) of sodium hydride (56.6% in mineral oil) was added. After the addition was completed, the reaction mixture was stirred at room temperature for 2 h, then heated to 60 °C for 16 h. The mixture was cooled and then poured into 500 ml of ice water. The aqueous layer was saturated with sodium chloride and extracted with three 250-ml portions of chloroform. The combined extract was washed twice with saturated sodium chloride solution and dried over sodium sulfate. Evaporation of the solvent gave 32.6 g of an oil, which was purified by chromatography on 900 g of silica gel packed in hexane. Elution with hexane containing 2% ether, and gradually increasing to 15% ether, gave 5.5 g of an isomeric mixture. This was purified by repeated recrystallization from pentane to give 2.4 g (10.2%) of the less polar furanone **1** as yellow crystals: mp 129–137 °C; NMR ($CCl_4$) δ 1.04 (s, 6 H), 1.71 (s, 3 H), 2.01 (s, 3 H), 2.40 (s, 3 H), 5.88 (m, 1 H), 6.1 (d, $J$ = 16 Hz, 1 H), 6.3 (d, $J$ = 16 Hz, 1 H), 6.37 (d, $J$ = 12 Hz, 1 H), and 6.60 (d, $J$ = 12 Hz, 1 H); mass spectrum *m/e* 298 ($M^+$), 283, 265, and 255; uv $\lambda_{max}$ (2-propanol) (ε) 388 nm (39 130); ir ($CHCl_3$) 1747, 1587, and 1574 $cm^{-1}$. The material was found to be 94.5% isomerically pure by liquid chromatographic analysis.

Anal. Calcd for $C_{20}H_{26}O_2$: C, 80.50; H, 8.78. Found: C, 80.54; H, 8.96.

**(*Z*)-4-Methyl-5-[5-(2,6,6-trimethylcyclohexen-1-yl)-3-methyl-2(*E*),4(*E*)-pentadienylidene]-2(5*H*)-furanone (2).** The mother liquors from the above pentane recrystallization were combined and stored at −20 °C for 3 days. The resulting crystals were filtered and the two crystal forms were separated manually. Repeated recrystallization of the lower melting, more polar substance from cold pentane gave 350 mg of **2** as yellow crystals: mp 90–95 °C; NMR ($CCl_4$) δ 1.02 (s, 6 H), 1.21 (s, 3 H), 1.99 (s, 3 H), 2.18 (s, 3 H), 5.81 (m, 1 H), 6.01 (d, $J$ = 12 Hz, 1 H), 6.24 (s, 2 H), and 6.53 (d, $J$ = 12 Hz, 1 H); mass spectrum *m/e* 298 ($M^+$), 283, and 265; uv $\lambda_{max}$ (2-propanol) (ε) 385 nm (26 820) and 242 (7900); ir ($CHCl_3$) 1750 and 1575 $cm^{-1}$.

Anal. Calcd for $C_{20}H_{26}O_2$: C 80.50; H, 8.78. Found: C, 80.60; H, 8.79.

**Registry No.**—**1**, 60305-11-5; **2**, 10035-29-7; **3**, 55177-16-7; **4**, 3917-41-7; **5a**, 6124-79-4; **5b**, 60270-03-3; **5c**, 60270-04-4; triphenylphosphine, 603-35-0.

**Supplementary Material Available.** Tables of positional and thermal parameters for the structure of **1** (3 pages). Ordering information is given on any current masthead page.

## References and Notes


(1) Compounds **1** and **2** are named as derivatives of 2(5*H*)-furanone. However, because of their relationship to retinoic acid, this numbering system has been employed in this paper for purposes of discussion.
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## Carbohydrate Thio Ortho Esters. Synthesis and Characterization


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Carbohydrate ortho esters have been used extensively during the last 10 years for synthesis of 1,2-trans glycosides.[1]