to maintain a temperature under 25 °C. After ca. 30 min, 250 mL of 6 N hydrochloric acid was added, and the resulting solution was cooled in ice 2 h to give 430 mg of a flavonoid substance: mp 210 °C (positive $FeCl_3$ test and red color with Mg–HCl);[16] IR (KBr) 1705 (CO), and ca. 1645 cm^{-1} (flavonoid CO).

ω-Methoxyphloroacetophenone Tris(3,4-dimesyloxybenzoate) (14). To 1.98 g of ω-methoxyphloroacetophenone in 30 mL of reagent pyridine was added rapidly 9.84 g of protocatechuyl chloride dimesylate.[11b] The reaction mixture stood at room temperature 3 days. The heterogeneous mixture then was added slowly with vigorous stirring to 1.5 L of 6 N hydrochloric acid containing 1.5 kg of ice. The precipitate was collected, washed successively with 500 mL of 1 N hydrochloric acid and 500 mL of water, and dried in vacuo over P_2O_5. Recrystallization from the minimal quantity of ethanol–acetone (95/5 vol) gave the title ester in a 10.5-g (97%) yield, mp 80 °C. Anal. Calcd for $C_{36}H_{34}O_{26}S_6$: C, 40.22; H, 3.19. Found: C, 40.09; H, 3.41.

Attempted rearrangement of **14** in 50 mL of pyridine containing 5.6 g of potassium hydroxide at room temperature gave only water soluble products. No flavonoids could be detected.

ω-Benzoyloxyphloroacetophenone Tris(3,4-dimesyloxybenzoate) (15). ω-Benzoyloxyphloroacetophenone[21] (2.88 g) was reacted with 9.84 g of protocatechuyl chloride dimesylate,[11b] as described in the preceding section. Recrystallization of crude product from ethanol–acetone (95/5 vol) gave (10.3 g, 89%) mp 120 °C. Anal. Calcd for $C_{42}H_{36}O_{27}S_6$: C, 43.28; H, 3.11; S, 16.49. Found: C, 43.09; H, 3.38; S, 16.22.

Rearrangement of **15** (11.64 g) in 30 mL of glacial acetic acid containing 10 g of anhydrous potassium acetate at reflux for 48 h gave a red solution, which upon cooling set to a semisolid mass. Solution of the latter in 100 mL of acetic acid–sulfuric acid (20 mL), with removal of inorganic salts by filtration, gave a reddish orange filtrate which was heated gently for 2 h, diluted with 250 mL of water, and cooled in an ice chest overnight. A light yellow solid crystallized at the surface and was collected (negative $FeCl_3$ and Mg–HCl[16] tests, positive blue fluorescence in concentrated H_2SO_4): IR (KBr) 1665 cm^{-1} (flavonoid CO). This substance in 15 mL of dimethyl sulfoxide was added to potassium hydroxide (1 g) in 20 mL of water, permitted to stand 4 h at room temperature, added to 100 mL of 6 N hydrochloric acid, and cooled in an ice chest. The precipitated product (110 mg) gave positive $FeCl_3$ and Mg–HCl[16] tests.

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Registry No.—**1**, 55317-02-7; **2**, 6665-74-3; **3**, 65982-77-6; **4**, 65982-78-7; **5**, 603-61-2; **6**, 65982-79-8; **7**, 5150-31-2; **8**, 65982-80-1; **9**, 65982-81-2; **10**, 65982-82-3; **11**, 22105-21-1; **12**, 66008-59-1; **13**, 65982-83-4; **14**, 65982-84-5; **15**, 65982-85-6; benzoic anhydride, 93-97-0; isovanillic acid mesylate, 65982-86-7; piperonylic anhydride, 6938-53-0; 3,4-diphenylmethylenedioxybenzoic acid, 5693-25-4; mesyl chloride, 124-63-0; protocatechuyl chloride diacetate, 57929-25-6.

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Synthesis and Molecular Structure of *exo*-7-Phenyl-5,7-dimethyl-6,8-dioxabicyclo[3.2.1]octane

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The dimer of methyl vinyl ketone, when treated with phenylmagnesium bromide, was converted to the exo and endo isomers of 7-phenyl-5,7-dimethyl-6,8-dioxabicyclo[3.2.1]octane. The x-ray crystallographic examination of the exo isomer provides the first detailed structural data for this interesting bicyclic ketal series. The method of synthesis and the x-ray structural data are provided.

From the observation that 6,8-dioxabicyclo[3.2.1]octane constitutes the major structural framework of the aggregating sex pheromones for three pernicious bark beetles (brevicomin (**2**), (*Dendroctonus brevicomis*),[1] frontalin (**3**), (*D. frontalis*),[2] and multistriatin (**4**), (*Scolytus multistriatus*)[3]) has evolved an interest in the detailed structures of bicyclic ketals in this series. The additional realization that other natural products have this basic skeletal system has resulted in the motivation for a systematic analysis of these structures.[4]

We were most fortunate that as part of a general investigation directed toward syntheses in this series, a suitable solid sample, *exo*-7-phenyl-5,7-dimethyl-6,8-dioxabicyclo[3.2.1]octane (**6**), was available. Addition of the dimer **5** of methyl vinyl ketone to a solution of phenylmagnesium bromide re-

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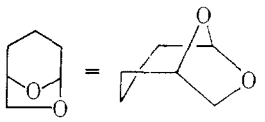
Table I. Bond Angles (deg) with Standard Deviations in Parentheses

C(2)–C(1)–O(8)	109.1 (3)	O(6)–C(7)–C(10)	109.3 (3)
C(2)–C(1)–C(7)	116.9 (4)	O(6)–C(7)–C(11)	109.7 (3)
C(2)–C(1)–H1	109 (2)	C(10)–C(7)–C(11)	109.0 (3)
O(8)–C(1)–C(7)	100.3 (3)	C(5)–O(6)–C(7)	107.9 (3)
O(8)–C(1)–H1	108 (2)	C(5)–C(9)–H9(1)	115 (2)
C(7)–C(1)–H1	113 (2)	C(5)–C(9)–H9(2)	107 (2)
C(1)–C(2)–C(3)	112.2 (4)	C(5)–C(9)–H9(3)	114 (2)
C(1)–C(2)–H2(1)	105 (2)	H9(1)–C(9)–H9(2)	103 (3)
C(1)–C(2)–H2(2)	110 (2)	H9(1)–C(9)–H9(3)	110 (3)
C(3)–C(2)–H2(1)	108 (2)	H9(2)–C(9)–H9(3)	107 (3)
C(3)–C(2)–H2(2)	112 (2)	C(7)–C(10)–H10(1)	112 (3)
H2(1)–C(2)–H2(2)	109 (3)	C(7)–C(10)–H10(2)	114 (2)
C(2)–C(3)–C(4)	112.8 (4)	C(7)–C(10)–H10(3)	118 (2)
C(2)–C(3)–H3(1)	108 (2)	H10(1)–C(10)–H10(2)	106 (3)
C(2)–C(3)–H3(2)	110 (2)	H10(1)–C(10)–H10(3)	100 (3)
C(4)–C(3)–H3(1)	114 (2)	H10(2)–C(10)–H10(3)	106 (3)
C(4)–C(3)–H3(2)	110 (2)	C(7)–C(11)–C(12)	122.4 (4)
H3(1)–C(3)–H3(2)	100 (3)	C(7)–C(11)–C(16)	120.3 (4)
C(3)–C(4)–C(5)	111.3 (4)	C(12)–C(11)–C(16)	117.3 (4)
C(3)–C(4)–H4(1)	109 (2)	C(11)–C(12)–C(13)	121.7 (4)
C(3)–C(4)–H4(2)	112 (2)	C(11)–C(12)–H12	120 (2)
C(5)–C(4)–H4(1)	104 (2)	C(13)–C(12)–H12	119 (2)
C(5)–C(4)–H4(2)	112 (2)	C(12)–C(13)–C(14)	119.8 (4)
H4(1)–C(4)–H4(2)	108 (3)	C(12)–C(13)–H13	121 (2)
C(4)–C(5)–O(8)	109.7 (3)	C(14)–C(13)–H13	119 (2)
C(4)–C(5)–O(6)	108.0 (3)	C(13)–C(14)–C(15)	119.2 (5)
C(4)–C(5)–C(9)	115.5 (4)	C(13)–C(14)–H14	116 (2)
O(8)–C(5)–O(6)	104.1 (3)	C(15)–C(14)–H14	124 (2)
O(8)–C(5)–C(9)	109.0 (4)	C(14)–C(15)–C(16)	121.2 (4)
O(6)–C(5)–O(9)	110.0 (3)	C(14)–C(15)–H15	118 (2)
C(1)–O(8)–C(5)	102.5 (3)	C(16)–C(15)–H15	121 (2)
C(1)–C(7)–O(6)	100.7 (3)	C(11)–C(16)–C(15)	120.8 (4)
C(1)–C(7)–C(10)	115.9 (4)	C(11)–C(16)–H16	115 (2)
C(1)–C(7)–C(11)	111.9 (3)	C(15)–C(16)–H16	124 (2)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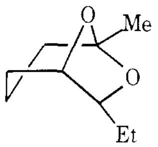
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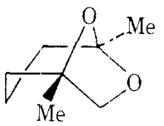
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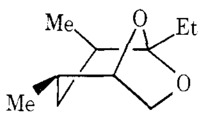
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sulted in the formation of **6** and the endo isomer **7** in the ratio of 3:1. It is important to emphasize, at this point, that the expected tertiary alcohol was not formed. Indeed, we have observed that for the addition of any Grignard or organolithium reagent to **5**, even in the absence of acid (other than water) during workup, only the ketal is isolated.[5] The exo isomer **6** crystallized from the reaction mixture and could be recrystallized from ethanol-water. Crystals suitable for x-ray structure analysis were obtained by sublimation.

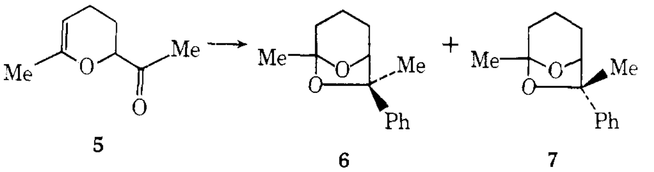
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Table II. Torsion Angles in Degrees

H1–C(1)–C(7)–C(11)	38	O(8)–C(1)–C(2)–C(3)	−55.7
H1–C(1)–C(7)–C(10)	88	C(1)–O(8)–C(5)–O(6)	39.8
C(5)–O(6)–C(7)–C(11)	101.7	O(8)–C(5)–O(6)–C–(7)	−13.2
C(5)–O(6)–C(7)–C(10)	−138.9	C(5)–O(6)–C(7)–C(1)	−16.4
C(2)–C(1)–C(7)–C(11)	165.9	O(6)–C(7)–C(1)–O(8)	40.1
C(2)–C(1)–C(7)–C(10)	40.1	C(7)–C(1)–O(8)–C(5)	−49.7
O(8)–C(1)–C(7)–C(11)	−76.3	O(6)–C(7)–C(1)–C(2)	−77.6
O(8)–C(1)–C(7)–C(10)	157.9	C(7)–C(1)–C(2)–C(3)	57.2
C(7)–O(6)–C(5)–C(9)	−129.8	C(7)–O(6)–C(5)–C(4)	103.4
C(1)–O(8)–C(5)–C(9)	157.1	O(6)–C(5)–C(4)–C(3)	−54.8
C(3)–C(4)–C(5)–C(9)	−178.3	C(16)–C(11)–C(7)–C(1)	−58.7
C(1)–C(2)–C(3)–C(4)	36.6	C(16)–C(11)–C(7)–O(6)	−169.5
C(2)–C(3)–C(4)–C(5)	−37.2	C(16)–C(11)–C(7)–C(10)	70.9
C(3)–C(4)–C(5)–O(8)	58.0	C(12)–C(11)–C(7)–C(1)	122.8
C(4)–C(5)–O(8)–C(1)	−75.5	C(12)–C(11)–C(7)–O(6)	12.0
C(5)–O(8)–C(1)–C(2)	73.7	C(12)–C(11)–C(7)–C(10)	−107.7

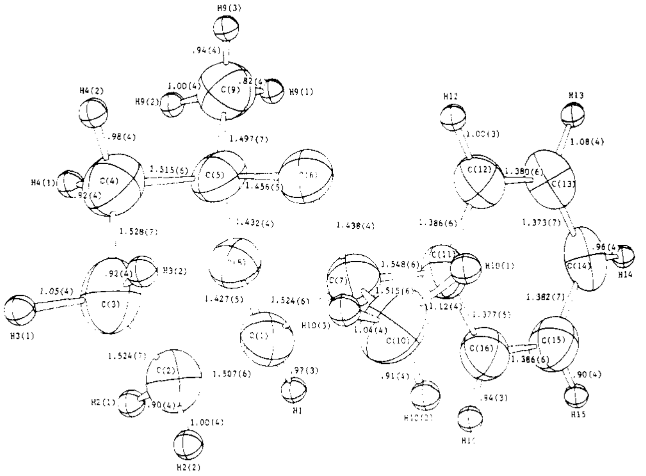

Figure 1. ORTEP drawing of *exo*-7-phenyl-5,7-dimethyl-6,8-dioxabicyclo[3.2.1]octane. The hydrogen atoms are represented by arbitrary spheres and the probability level for the thermal ellipsoids is 0.5.

The details of the x-ray determination are presented in the Experimental Section. An ORTEP drawing of **6**, with measured bond lengths, is presented in Figure 1. Tables I–IV provide the important structural data, including bond angles, dihedral angles, and coordinate system. The stereoview is presented in Figure 2.

Experimental Section

Preparation of 6 and 7. To an ether solution of phenylmagnesium bromide (0.01 mol) was slowly added 1.4 g (0.01 mol) of **5**. The reaction mixture was stirred and at various time intervals 10-mL portions were analyzed by GLC for **5**. When this had been consumed, water was carefully added, to hydrolyze the salts. the ether solution was filtered, dried, and reduced in volume to give the crude product in about 90% yield. GLC analysis (SE-30) indicated two products in the ratio of 3:1

Table III. Equations of Planes and Dihedral Angles

	A^a	B	C	D	Σ
(1) C(7),C(11),C(12), C(13),C(14),C(15),C(16)	−0.2961	0.7632	0.5729	13.465	3.6×10^{-4}
(2) C(1),C(5),C(7),O(6)	0.4494	0.2907	−0.8448	5.514	2.5×10^{-2}
(3) C(1),C(5),O(8)	0.1240	0.8835	−0.4517	13.890	
(4) C(1),C(2),C(4),C(5)	−0.4739	0.7564	0.4510	10.021	1.5×10^{-4}
(5) C(2),C(3),C(4)	−0.2017	0.9793	−0.0178	13.436	
(6) C(1),C(2),O(8)	−0.8790	0.4730	0.0609	0.011	
(7) C(2),C(3),C(5),O(8)	−0.0448	0.9686	0.2447	15.894	6.2×10^{-2}
(8) C(3),C(4),C(5)	−0.7108	0.6712	0.2105	6.218	

Dihedral Angles, deg

(1)–(2)	66.8	(4)–(5)	34.1
(2)–(3)	46.0	(6)–(7)	59.2
(2)–(4)	68.0	(7)–(8)	42.8
(3)–(4)	66.1		

[a] The equation of the plane is $Ax + By + Cz - D = 0$, where A, B, and C are direction cosines, D is the perpendicular distance from the plane to the origin, and is the sum of the squares of the deviations of the atoms from the least-square plane. The coordinate system is described by x along a, y along the b, and z along the c axes.

Table IV. Positional and Thermal Parameters and Standard Deviations[a]

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0.36049 (16)	0.65013 (16)	0.5479 (6)	0.00128 (8)	0.00169 (9)	0.0237 (11)	0.00001 (6)	−0.0003 (3)	0.0010 (3)
C(2)	0.34420 (20)	0.61410 (19)	0.6984 (7)	0.00234 (11)	0.00184 (9)	0.0273 (14)	−0.00027 (8)	−0.0015 (3)	0.0011 (3)
C(3)	0.28513 (19)	0.60192 (19)	0.6948 (7)	0.00214 (11)	0.00206 (10	0.0284 (14)	−0.00044 (9)	0.0016 (3)	0.0013 (3)
C(4)	0.26374 (17)	0.59651 (18)	0.5083 (7)	0.00156 (9)	0.00189 (10)	0.0263 (13)	−0.00017 (8)	0.0006 (3)	−0.0002 (3)
C(5)	0.28938 (15)	0.63526 (17)	0.3829 (6)	0.00116 (7)	0.00182 (9)	0.0224 (11)	−0.00010 (7)	−0.0001 (2)	−0.0006 (3)
O(8)	0.34489 (11)	0.62738 (11)	0.3824 (4)	0.00132 (5)	0.00168 (6)	0.0238 (7)	0.00005 (5)	0.0006 (2)	−0.0003 (2)
C(7)	0.33251 (15)	0.70354 (16)	0.5360 (6)	0.00111 (7)	0.00156 (8)	0.0202 (10)	0.00002 (6)	−0.0001 (2)	−0.0002 (3)
O(6)	0.28280 (10)	0.68789 (10)	0.4579 (4)	0.00110 (5)	0.00137 (5)	0.0269 (8)	0.00001 (4)	0.0002 (2)	−0.0002 (2)
C(9)	0.26989 (20)	0.63419 (19)	0.1965 (7)	0.00222 (10)	0.00216 (10)	0.0281 (14)	0.00001 (9)	−0.0004 (3)	−0.0009 (3)
C(10)	0.32249 (18)	0.73094 (18)	0.7108 (7)	0.00186 (9)	0.00233 (10)	0.0243 (12)	−0.00027 (8)	−0.0007 (3)	−0.0012 (3)
C(11)	0.36092 (16)	0.74130 (15)	0.4105 (6)	0.00137 (8)	0.00110 (7)	0.0211 (11)	0.00017 (6)	0.0006 (3)	−0.0003 (2)
C(12)	0.33643 (17)	0.76395 (17)	0.2653 (7)	0.00149 (8)	0.0280 (12)	0.00016 (7)	0.00016 (7)	0.0000 (3)	0.0003 (3)
C(13)	0.36245 (20)	0.79918 (18)	0.1545 (6)	0.00216 (11)	0.00156 (9)	0.0233 (12)	0.00041 (8)	0.0005 (3)	0.0010 (3)
C(14)	0.41411 (20)	0.81190 (17)	0.1881 (7)	0.00220 (11)	0.00129 (8)	0.0274 (14)	0.00000 (8)	0.0019 (3)	0.0006 (3)
C(15)	0.43906 (17)	0.78943 (18)	0.3304 (7)	0.00153 (9)	0.00162 (9)	0.0287 (13)	−0.00005 (7)	0.0010 (3)	−0.0002 (3)
C(16)	0.41319 (17)	0.75512 (17)	0.4422 (6)	0.00162 (9)	0.00149 (8)	0.0206 (11)	0.00003 (7)	0.0000 (3)	0.0002 (3)
H1	0.3990 (12)	0.6530 (12)	0.547 (4)	3.42					
H2(1)	0.3629 (13)	0.5814 (14)	0.677 (4)	4.46					
H2(2)	0.3549 (12)	0.6284 (13)	0.810 (4)	4.46					
H3(1)	0.2781 (13)	0.5708 (13)	0.774 (4)	4.45					
H3(2)	0.2667 (13)	0.6277 (13)	0.756 (4)	4.45					
H4(1)	0.2743 (13)	0.5609 (13)	0.459 (4)	3.98					
H4(2)	0.2262 (13)	0.5988 (13)	0.505 (4)	3.98					
H9(1)	0.2879 (14)	0.6534 (14)	0.120 (4)	4.73					
H9(2)	0.2750 (13)	0.5992 (14)	0.152 (4)	4.73					
H9(3)	0.2362 (14)	0.6414 (13)	0.186 (4)	4.73					
H10(1)	0.3020 (13)	0.7668 (13)	0.693 (4)	4.38					
H10(2)	0.3523 (13)	0.7393 (13)	0.773 (4)	4.38					
H10(3)	0.2992 (13)	0.7139 (13)	0.795 (4)	4.38					
H12	0.3005 (13)	0.7567 (12)	0.243 (4)	3.74					
H13	0.3436 (12)	0.8165 (13)	0.045 (4)	4.10					
H14	0.4304 (13)	0.8345 (12)	0.106 (5)	3.91					
H15	0.4731 (12)	0.7978 (12)	0.349 (4)	4.03					
H16	0.4286 (11)	0.7405 (12)	0.552 (4)	3.47					

[a] The form of the anisotropic temperature expression is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

(peak areas). The mass spectral molecular weights and the NMR spectra of the two products were compatable with structures **6** and **7**, respectively. Calcd for **6**, $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.93; H, 8.35. Found for **7**, $C_{14}H_{18}O_2$: C, 77.10; H, 8.14.

The major product of this reaction crystallized from the reaction mixture and could be recrystallized from ethanol–water, mp 54–55 °C. Room temperature sublimation was effective for purification. However, crystals most suitable for x-ray analysis were obtained by slow crystallization (ca. 1 month) from the sublimate.

The NMR spectrum ($CDCl_3$) exhibited a multiplet centered at δ 7.2 (5 H, aromatic), a singlet at δ 4.3 (1 H, methine), a multiplet centered at δ 1.7 (6 H, ring protons), a singlet at δ 1.8 (3 H, methyl), and a singlet at δ 1.4 (3 H, methyl).

The density of a crystal, measured by floation in H_2O/H_2SO_4, was 1.173 g/cm³.

Crystallographic Data Collection. A needle-shaped crystal fragment was sealed in a glass capillary to prevent sublimation during exposure to x rays. Preliminary Weissenberg and Buerger precession photographs indicated a tetragonal space group with systematic absences of hkl, $h + k + l \neq 2n$; $hk0$, $h(k) \neq 2n$; and $00l$, $l \neq 4n$.

Unit cell dimensions, refined by least squares from 14 independent 2θ values, obtained with a GE XRD-490 diffractometer using Ni filtered Cu Kα radiation and a scintillation counter, are: $a = b = 25.433(4)$, $c = 7.498$ (2) Å, and space group $I4_1/a$.

The crystal fragment was mounted along the c axis which was roughly parallel to its long dimension. Its approximate dimensions

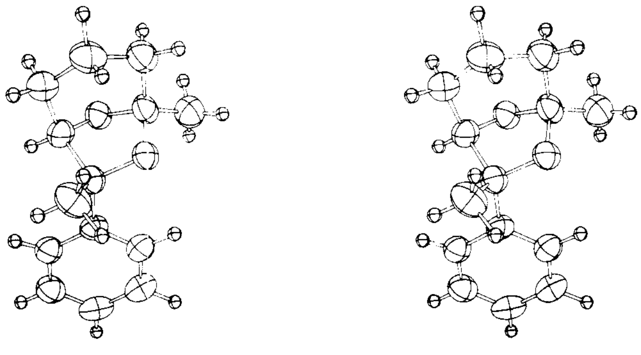

Figure 2. Stereoview of *exo*-7-Phenyl-5,7-dimethyl-6,8-dioxabicyclo[3.2.1]octane.

were 1.4 mm in length and 0.25 mm in average diameter, but no clearly defined faces could be discerned. Intensity data were collected out to a 2θ of 120° using automatic θ–2θ step scans with backgrounds counted at both extremes of the scan range. Three standard reflections were measured at 50 reflection intervals and showed no significant change. Of the 2043 reflections scanned, 1061 were considered observed based on the criterion $I > 3\sigma(I)$; unobserved data were not included in structure refinement. Lorentz and polarization corrections were applied in the normal manner,[6] and weights were calculated according to the method of Stout and Jensen:[7] $w(F) = [(k/4LpI)\,(\sigma^2(I) + (0.03I)^2)]^{-1}$. Scattering factors for non-hydrogen atoms were taken from Cromer and Mann;[8] the scattering factor curve for hydrogen was that of Stewart, Davidson, and Simpson.[9] No corrections were made for absorption and extinction.

Structure Analysis and Refinement. The structure was solved by direct methods using the program MULTAN.[6] The positions of the non-hydrogen atoms were first refined isotropically then anisotropically using full-matrix least-squares procedures minimizing $\Sigma w(\Delta F)^2$. A difference Fourier map revealed all the hydrogen atoms except those of the two methyl groups. The hydrogen atoms were assigned the refined isotropic temperature factors of the atoms to which they are bound and after three additional cycles of refinement a second difference Fourier map gave the positions of the methyl hydrogens. Subsequent refinement of positional parameters for all atoms and anisotropic thermal parameters for non-hydrogen atoms produced a final R factor of 5.5% $[R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|]$. The weighted R_w was 6.5% ($R_w = [\Sigma w(\Delta F)^2]^{1/2}/[\Sigma w F_o{}^2]^{1/2}$, and S, the standard deviation of an observation of unit weight, was calculated to be 2.16 ($S = [\Sigma w \Delta F^2/(m - n)]^{1/2}$, where m is the number of observations and n is the number of parameters).

Discussion

The results of this study provide a precise knowledge of the basic atomic skeletal features for this series, which should be useful in other studies. For example, Gore et al. recently reported on the analysis of frontalin and multistriatin by the lanthanide shift reagent experiment.[10] As necessary input data for the study it was necessary to rely on structural coordinate data generated without benefit of x-ray results. The unusually long europium–oxygen distances[11] associated with the lowest agreement factors for this work may be a consequence of the derived coordinate system.[12] Also, some NMR coupling constant correlations with C-7 substitution[13] have not yet been rationalized. It would appear that ring deformation as a result of increasing size of endo-C-7 substituents could qualitatively be invoked; however, a quantitative explanation is not yet possible. Because of the intimate relationship of coupling constants to dihedral angles, the x-ray data reported here may find application in studies of the bicyclic ketal series which rely on coupling constant analyses.

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Registry No.—**5,** 28450-02-4; **6,** 65899-46-9; **7,** 65899-47-0; phenyl bromide, 108-86-1.

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