

Structures of 4',5'-Dihydrospiro[anthracene-9(10H),2'(3'H)-furan]-10-one (1), and 3',4',5',6'-Tetrahydrospiro[anthracene-9(10H),2'-[2H]pyran]-10-one (2)

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Abstract. (1), $C_{17}H_{14}O_2$, $M_r = 250.30$, monoclinic, $P2_1/c$, $a = 14.205(7)$, $b = 11.842(4)$, $c = 15.726(6)$ Å, $\beta = 98.52(4)^\circ$, $V = 2616(2)$ Å³, $Z = 8$, $D_x = 1.27$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu(\text{Mo } K\alpha) = 0.08$ mm⁻¹, $F(000) = 1056$, $T = 298$ K, final $R = 0.065$ for 2622 observed reflections. (2), $C_{18}H_{16}O_2$, $M_r = 264.32$, monoclinic, $P2_1/c$, $a = 15.163(2)$, $b = 11.888(2)$, $c = 15.280(3)$ Å, $\beta = 100.26(2)^\circ$, $V = 2710.3(8)$ Å³, $Z = 8$, $D_x = 1.30$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 0.08$ mm⁻¹, $F(000) = 1120$, $T = 296$ K, final $R = 0.040$ for 1650 observed reflections. The asymmetric units consist of two molecules. The five-membered furanoid rings in (1) adopt stable conformations whereas the six-membered pyranoid rings in (2) are under considerable strain.

Introduction. The two title compounds were synthesized as part of a study on the use of anthrone derivatives as redox catalysts (Pakkala & Brunow, 1986). The closure of the spiro ether ring attached to the anthracene system proved to be more difficult for the six-membered ring than for the five-membered ring. To ascertain if there were steric reasons for this difference in cyclization tendency, we carried out the crystal structure determination.

Experimental. The spiro compounds were prepared by alkylation of anthrahydroquinone in alkaline solution with 1,3-dibromopropane and 1,4-dibromobutane, respectively. The five-membered ring was formed directly in one reaction step, whereas the formation of the six-membered ring required a two-step procedure (Brunow, Pakkala & Pajunen, 1988).

(1), Transparent plate, crystal size $0.50 \times 0.30 \times 0.15$ mm, Nicolet P3 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, lattice parameters from

setting angles of 22 reflections with $9 < \theta < 20^\circ$, 4352 independent reflections collected with $3 < 2\theta < 50^\circ$, hkl range $h 0 \rightarrow 17$, $k 0 \rightarrow 15$, $l -19 \rightarrow 19$, ω -scan technique, 2622 observed reflections with $I > 2\sigma(I)$, $R_{\text{int}} = 0.016$, $\sigma(I)$ from counting statistics, L_p corrections, two standard reflections, no significant variation. The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1985) and refined by full-matrix least squares using *SHELX76* (Sheldrick, 1976) minimizing $\sum w(|F_o| - |F_c|)^2$. C(16)B is disordered between two positions. All H atoms were found in a difference map except the disordered H atoms, which were placed at calculated positions. Final $R = 0.065$, $wR = 0.071$, $w = [\sigma^2(F) + 0.0018F^2]^{-1}$, $S = 1.78$, 385 parameters refined, max. and min. heights in final difference Fourier synthesis 0.42 and -0.25 e Å⁻³, $(\Delta/\sigma)_{\text{max}} = 0.64$. Scattering factors from *International Tables for X-ray Crystallography* (1974). C atoms of the spiro ether ring have large thermal parameters.

(2), Transparent plate, crystal size $0.15 \times 0.25 \times 0.10$ mm, Enraf-Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, lattice parameters from setting angles of 25 reflections with $14 < \theta < 17^\circ$. 3975 reflections measured with $2\theta < 46^\circ$, hkl range $h 0 \rightarrow 16$, $k 0 \rightarrow 13$, $l -16 \rightarrow 16$, variable rate ω - 2θ scan, ω scan width $(0.5 + 0.34 \tan \theta)^\circ$. Two standard reflections, no significant variation. 1650 observed reflections with $I > 3\sigma(I)$, $\sigma(I)$ from counting statistics. Structure solved by direct methods and refined by full-matrix least squares minimizing $\sum w(|F_o| - |F_c|)^2$. H atoms were located geometrically and their positions were refined in least squares, their isotropic thermal parameters were held fixed at $U = 0.05$ Å². Final $R = 0.040$, $wR = 0.038$, $w = 4F_o^2/\sigma^2(F_o)^2$, $S = 1.25$. 457 parameters refined, max. and min. heights in final difference Fourier synthesis 0.27

Table 1. Final atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for (1)
$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	Molecule A				Molecule B			
	x	y	z	U_{eq}	x	y	z	U_{eq}
O(1)	5117 (2)	2909 (3)	6885 (2)	98 (2)	2175 (2)	7478 (3)	9698 (2)	83 (2)
O(2)	2688 (2)	1767 (2)	4026 (2)	67 (2)	-655 (2)	5603 (2)	7437 (2)	72 (2)
C(1)	4499 (3)	2685 (4)	6280 (2)	67 (2)	1531 (3)	7138 (3)	9153 (2)	59 (2)
C(2)	4040 (2)	1555 (3)	6192 (2)	59 (2)	1722 (3)	6654 (3)	8330 (2)	52 (2)
C(3)	4086 (3)	846 (4)	6903 (3)	81 (3)	2594 (3)	6864 (3)	8053 (3)	66 (2)
C(4)	3631 (4)	-188 (4)	6842 (3)	88 (3)	2750 (3)	6492 (4)	7246 (3)	77 (3)
C(5)	3126 (3)	-507 (4)	6063 (3)	79 (3)	2046 (3)	5904 (4)	6730 (3)	78 (3)
C(6)	3076 (3)	178 (3)	5348 (3)	65 (2)	1182 (3)	5671 (3)	7010 (2)	63 (2)
C(7)	3530 (2)	1227 (3)	5405 (2)	53 (2)	1011 (2)	6050 (3)	7811 (2)	50 (2)
C(8)	3540 (2)	1966 (3)	4625 (2)	54 (2)	91 (3)	5768 (3)	8146 (2)	55 (2)
C(9)	3604 (2)	3209 (3)	4862 (2)	50 (2)	-192 (3)	6695 (3)	8723 (2)	56 (2)
C(10)	3195 (3)	4028 (3)	4286 (2)	62 (3)	-1135 (3)	6929 (4)	8776 (3)	76 (3)
C(11)	3299 (3)	5160 (3)	4493 (3)	72 (3)	-1366 (4)	7720 (4)	9359 (3)	96 (3)
C(12)	3816 (3)	5492 (3)	5261 (3)	73 (3)	-670 (4)	8279 (4)	9897 (3)	99 (4)
C(13)	4230 (3)	4693 (4)	5838 (3)	66 (3)	268 (4)	8071 (4)	9848 (3)	78 (3)
C(14)	4119 (2)	3541 (3)	5636 (2)	54 (2)	518 (3)	7281 (3)	9254 (2)	55 (2)
C(15)	4373 (3)	1630 (3)	4132 (3)	72 (3)	177 (4)	4623 (4)	8632 (3)	74 (3)
C(16)*	3926 (4)	856 (5)	3446 (3)	106 (3)	-145 (12)	3801 (10)	7953 (9)	83 (9)
C(161)*	—	—	—	—	-611 (19)	3931 (18)	8253 (18)	190 (19)
C(17)	2941 (4)	1343 (4)	3226 (3)	89 (3)	-987 (5)	4462 (5)	7423 (4)	103 (4)

*Population parameter 0.5 for C(16)B and C(161)B.

Table 2. Final atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA} \times 10^3$) for (2)
$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	Molecule A				Molecule B			
	x	y	z	U_{eq}	x	y	z	U_{eq}
O(1)	4492 (2)	2291 (4)	8192 (2)	89 (1)	9471 (2)	767 (4)	7401 (2)	85 (1)
O(2)	1798 (2)	863 (3)	9818 (2)	52 (1)	6754 (2)	1280 (3)	4595 (2)	57 (1)
C(1)	3881 (3)	2025 (4)	8577 (3)	57 (1)	8873 (3)	945 (4)	6775 (3)	56 (1)
C(2)	4053 (3)	1523 (4)	9474 (3)	46 (1)	7937 (3)	1125 (4)	6896 (3)	49 (1)
C(3)	4908 (3)	1599 (4)	9992 (3)	58 (1)	7774 (3)	1397 (4)	7744 (3)	62 (1)
C(4)	5063 (3)	1182 (5)	10838 (3)	66 (1)	6923 (4)	1632 (5)	7866 (3)	73 (1)
C(5)	4395 (3)	665 (4)	11185 (3)	62 (1)	6226 (3)	1606 (5)	7157 (3)	77 (1)
C(6)	3548 (3)	572 (4)	10666 (3)	52 (1)	6373 (3)	1327 (4)	6318 (3)	61 (1)
C(7)	3364 (3)	1005 (4)	9814 (3)	41 (1)	7234 (3)	1103 (4)	6172 (3)	46 (1)
C(8)	2451 (3)	840 (4)	9243 (3)	44 (1)	7403 (3)	733 (4)	5266 (3)	46 (1)
C(9)	2236 (3)	1772 (4)	8550 (3)	41 (1)	8341 (3)	1084 (4)	5137 (3)	44 (1)
C(10)	1362 (3)	2105 (4)	8224 (3)	52 (1)	8528 (3)	1332 (4)	4297 (3)	57 (1)
C(11)	1192 (3)	2903 (4)	7557 (4)	67 (1)	9398 (3)	1590 (5)	4193 (3)	67 (1)
C(12)	1864 (4)	3341 (5)	7183 (3)	75 (1)	10088 (3)	1558 (5)	4912 (4)	65 (1)
C(13)	2736 (3)	3031 (5)	7502 (3)	67 (1)	9921 (3)	1310 (4)	5736 (3)	58 (1)
C(14)	2934 (3)	2256 (4)	8195 (3)	51 (1)	9044 (3)	1083 (4)	5861 (3)	48 (1)
C(15)	2452 (3)	-313 (4)	8771 (3)	49 (1)	7311 (3)	-560 (4)	5222 (3)	58 (1)
C(16)	1506 (4)	-720 (4)	8377 (4)	68 (1)	7220 (4)	-1004 (5)	4299 (4)	90 (3)
C(17)	961 (4)	-744 (5)	9110 (4)	96 (3)	6408 (5)	-447 (8)	3740 (5)	144 (4)
C(18)	1235 (5)	-43 (7)	9808 (4)	194 (3)	6168 (5)	637 (6)	4006 (5)	157 (3)

and -0.31 e \AA^{-3} , $(\Delta/\sigma)_{\text{max}} = 0.59$. Scattering factors from *International Tables for X-ray Crystallography* (1974). All calculations performed by Enraf-Nonius SDP-Plus package (Frenz, 1978).

Discussion. The final atomic parameters are given in Tables 1 and 2 and the bond lengths and angles in Table 3.* The conformation of molecules (1)B and

(2)A, together with the atom-labelling scheme, are shown in Figs. 1 and 2. The crystal packing of (1) is illustrated in Fig. 3 (Johnson, 1976).

In both structures the asymmetric unit consists of two crystallographically independent molecules. The bond lengths and angles are essentially identical in both compounds except for the spiro ether ring, which is disordered in molecule (2)B. The central ring in the anthrone part has a boat conformation and the angles between the planes of the outer phenyl rings are $28.5 (1)$, $29.6 (1)$, $26.0 (1)$ and $28.6 (1)^\circ$ for molecules (1)A, (1)B, (2)A and (2)B, respectively. The C atoms of the spiro ether rings have large thermal parameters, indicating that they are somewhat dis-

* Lists of structure factors, anisotropic thermal parameters and H-atom positions have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51439 (35 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Bond lengths (Å) and angles (°) with *e.s.d.*'s in parentheses

	Compound (1)		Compound (2)	
	A	B	A	B
O(1)—C(1)	1.225 (5)	1.225 (5)	1.224 (6)	1.214 (5)
O(2)—C(8)	1.440 (4)	1.433 (4)	1.436 (6)	1.443 (5)
O(2)—C(17)	1.448 (5)	1.430 (7)	—	—
O(2)—C(18)	—	—	1.373 (9)	1.378 (8)
C(1)—C(2)	1.486 (6)	1.478 (5)	1.475 (6)	1.479 (7)
C(1)—C(14)	1.477 (5)	1.480 (6)	1.476 (6)	1.474 (7)
C(2)—C(3)	1.391 (6)	1.395 (6)	1.396 (6)	1.400 (7)
C(2)—C(7)	1.394 (5)	1.397 (5)	1.391 (7)	1.393 (6)
C(3)—C(4)	1.381 (7)	1.392 (7)	1.365 (7)	1.365 (8)
C(4)—C(5)	1.377 (6)	1.379 (6)	1.370 (7)	1.373 (6)
C(5)—C(6)	1.380 (6)	1.391 (7)	1.388 (6)	1.380 (7)
C(6)—C(7)	1.397 (5)	1.392 (5)	1.381 (6)	1.389 (7)
C(7)—C(8)	1.508 (5)	1.517 (5)	1.512 (6)	1.517 (7)
C(8)—C(9)	1.517 (5)	1.517 (5)	1.527 (7)	1.528 (7)
C(8)—C(15)	1.559 (6)	1.552 (6)	1.549 (7)	1.544 (6)
C(9)—C(10)	1.394 (5)	1.382 (6)	1.388 (6)	1.394 (7)
C(9)—C(14)	1.382 (5)	1.396 (5)	1.396 (7)	1.393 (6)
C(10)—C(11)	1.382 (6)	1.384 (7)	1.383 (7)	1.391 (7)
C(11)—C(12)	1.375 (6)	1.372 (7)	1.358 (8)	1.376 (6)
C(12)—C(13)	1.380 (6)	1.368 (8)	1.376 (7)	1.360 (8)
C(13)—C(14)	1.404 (6)	1.404 (6)	1.395 (7)	1.403 (9)
C(15)—C(16)	1.485 (7)	1.466 (14)	1.532 (7)	1.489 (8)
C(15)—C(161)	—	1.442 (25)	—	—
C(16)—C(17)	1.506 (8)	1.563 (16)	1.506 (9)	1.520 (9)
C(161)—C(17)	—	1.476 (27)	—	—
C(17)—C(18)	—	—	1.359 (9)	1.418 (12)
C(8)—O(2)—C(17)	109.4 (3)	110.2 (3)	—	—
C(8)—O(2)—C(18)	—	—	118.3 (4)	119.5 (4)
O(1)—C(1)—C(2)	121.4 (4)	121.6 (4)	121.8 (4)	121.7 (4)
O(1)—C(1)—C(14)	122.1 (4)	121.6 (4)	121.9 (4)	122.2 (4)
C(2)—C(1)—C(14)	116.4 (3)	116.5 (3)	116.2 (4)	115.9 (4)
C(1)—C(2)—C(3)	120.1 (3)	119.4 (3)	119.6 (4)	118.7 (4)
C(1)—C(2)—C(7)	119.7 (3)	119.9 (3)	120.4 (4)	120.9 (4)
C(3)—C(2)—C(7)	120.1 (4)	120.5 (3)	120.0 (4)	120.2 (4)
C(2)—C(3)—C(4)	120.9 (4)	119.8 (4)	119.9 (5)	120.1 (4)
C(3)—C(4)—C(5)	118.8 (4)	119.8 (4)	121.0 (4)	120.1 (5)
C(4)—C(5)—C(6)	121.3 (4)	120.7 (4)	119.2 (4)	120.6 (5)
C(5)—C(6)—C(7)	120.2 (3)	120.2 (4)	121.3 (5)	120.5 (4)
C(2)—C(7)—C(6)	118.6 (4)	119.0 (3)	118.6 (4)	118.5 (4)
C(2)—C(7)—C(8)	119.6 (3)	119.7 (3)	120.9 (4)	120.0 (4)
C(6)—C(7)—C(8)	121.6 (3)	121.2 (3)	120.4 (4)	121.2 (4)
O(2)—C(8)—C(7)	109.2 (3)	109.6 (3)	107.7 (4)	108.2 (4)
O(2)—C(8)—C(9)	109.5 (3)	109.5 (3)	109.0 (4)	108.5 (4)
O(2)—C(8)—C(15)	105.0 (3)	105.0 (3)	111.1 (4)	111.9 (4)
C(7)—C(8)—C(9)	111.8 (3)	111.5 (3)	111.5 (4)	110.5 (4)
C(7)—C(8)—C(15)	110.8 (3)	110.8 (3)	107.9 (4)	107.4 (4)
C(9)—C(8)—C(15)	110.3 (3)	110.3 (3)	109.7 (4)	110.2 (4)
C(8)—C(9)—C(10)	120.8 (3)	121.8 (3)	121.9 (4)	121.5 (4)
C(8)—C(9)—C(14)	119.8 (3)	119.1 (3)	119.0 (4)	119.7 (4)
C(10)—C(9)—C(14)	119.3 (3)	119.0 (3)	119.0 (4)	118.6 (4)
C(9)—C(10)—C(11)	120.2 (3)	120.2 (4)	120.1 (5)	120.3 (4)
C(10)—C(11)—C(12)	120.6 (4)	121.0 (5)	121.2 (4)	120.3 (5)
C(11)—C(12)—C(13)	120.1 (4)	119.8 (5)	119.6 (5)	120.3 (5)
C(12)—C(13)—C(14)	119.7 (4)	120.1 (4)	120.6 (5)	120.3 (4)
C(1)—C(14)—C(9)	120.0 (3)	120.5 (3)	121.4 (4)	120.9 (4)
C(1)—C(14)—C(13)	119.7 (3)	119.6 (3)	119.1 (4)	118.8 (4)
C(9)—C(14)—C(13)	120.2 (3)	119.8 (4)	119.4 (4)	120.1 (4)
C(8)—C(15)—C(16)	104.2 (4)	103.2 (6)	112.6 (4)	112.7 (4)
C(8)—C(15)—C(161)	—	107.1 (10)	—	—
C(15)—C(16)—C(17)	102.3 (4)	100.8 (8)	108.3 (5)	107.9 (5)
C(15)—C(161)—C(17)	—	106.3 (16)	—	—
C(16)—C(17)—C(18)	—	—	116.1 (6)	117.3 (6)
O(2)—C(17)—C(16)	106.0 (3)	103.9 (6)	—	—
O(2)—C(17)—C(161)	—	108.3 (10)	—	—
O(2)—C(18)—C(17)	—	—	126.3 (6)	121.5 (6)

ordered and the rings are under considerable strain. The ring puckering was analysed by the method of Cremer & Pople (1975) using a program described by Boeyens

(1978). In compound (1), the ring puckering parameters are $Q = 0.349 (5) \text{ \AA}$ and $\varphi = 286.4 (6)^\circ$ for molecule A, and $Q = 0.400 (12) \text{ \AA}$, $\varphi = 282.4 (8)^\circ$ and $Q = 0.167 (19) \text{ \AA}$, $\varphi = 296 (2)^\circ$ for the disordered molecule B. The φ values are close to the values appropriate to a stable envelope ($\varphi = 288^\circ$) or a twist (half-chair) conformation ($\varphi = 306^\circ$).

In compound (2) the puckering parameters for the six-membered pyranoid ring are $Q = 0.528 (6) \text{ \AA}$, $\varphi = 133.8 (6)^\circ$, $\theta = 69.9 (6)^\circ$ for molecule A and

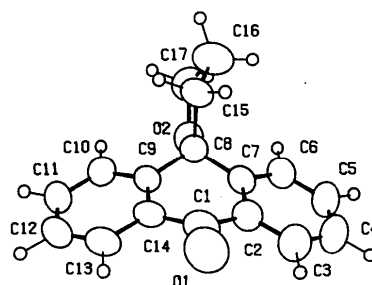


Fig. 1. Perspective view of molecule B for compound (1).

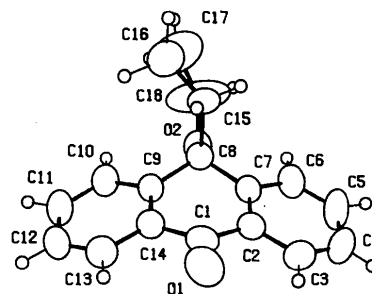


Fig. 2. Perspective view of molecule A for compound (2).

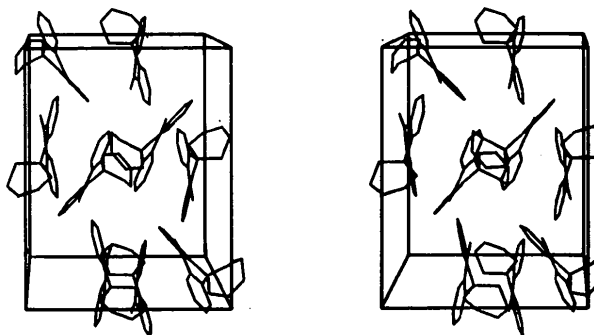


Fig. 3. Stereoscopic illustration of molecular packing for compound (2), b horizontal, c vertical.

$Q = 0.543(6) \text{ \AA}$, $\varphi = 137.4(7)^\circ$, $\theta = 71.9(6)^\circ$ for molecule *B*. The rings have a conformation between 3S_4 , 3E and 3B rather than corresponding to any stable conformation. Puckering analysis shows that the pyranoid ring is under considerable strain, while the strain in the furanoid ring is less because of the smaller deviation from the stable conformation.

The crystal packing does not reveal particularly short contacts.

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Functionalized Hydrocarbons with Condensed Ring Skeletons. II. A 3-Oxotricyclo[8.4.0.0^{2,7}]tetradec-8-ene

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Abstract. Tetramethyl 1,10-*trans*-1,2-*cisoid*-2,7-*cis*-1-methyl-3-oxotricyclo[8.4.0.0^{2,7}]tetradec-8-ene-5,5,12,12-tetracarboxylate, $C_{23}H_{30}O_9$, $M_r = 450.49$, triclinic, $P\bar{1}$, $a = 8.701(3)$, $b = 12.6690(10)$, $c = 12.7403(10) \text{ \AA}$, $\alpha = 114.300(10)$, $\beta = 99.127(10)$, $\gamma = 107.988(10)^\circ$, $V = 1149.71 \text{ \AA}^3$, $Z = 2$, $D_x = 1.301 \text{ Mg m}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.70930 \text{ \AA}$, $\mu = 0.09 \text{ mm}^{-1}$, $F(000) = 479.95$, room temperature, final $R = 0.044$ for 1937 observed reflections. The tricyclic compound has a ring skeleton closely related to the *ABC* rings in steroids. Rings *A* and *C* adopt a chair conformation with the methyl group axial at C(1), while ring *B* has a half-chair conformation. The relative stereochemistry is *trans* for the *AB* ring junction, *syn* between Me–C(1) and H–C(2) and *cis* for the *BC* ring junction (*T–S–C*).

Introduction. In an earlier communication (Michel, Proulx & Michel-Dewez, 1988), we have reported the conformational properties and the X-ray data of a

tricyclic molecule having a tridecane skeleton. The synthesis of this molecule (Bérubé & Deslongchamps, 1987) was part of a general study of transannular Diels–Alder reactions, which demonstrates that the transannular Diels–Alder reaction on a macrocyclic triene is a powerful strategy for the construction of complex polycyclic molecules.

During the course of this study, compound (1) (Fig. 1), a possible intermediate in corticoid synthesis, was prepared (Marinier & Deslongchamps, 1988). Macrocyclization of the allylic chloride (2) (Fig. 1) to give triene (3) was followed by transannular Diels–Alder reaction resulting in the formation of (4). The relative stereochemistry of four [C(10), C(1), C(2), C(7)] of the five asymmetric centers in tricycle (4) can be predicted (Lamothe, Ndibwami & Deslongchamps, 1988). With a *trans–cis* diene and a *cis* dienophile, the transannular Diels–Alder reaction is expected to give a tricycle having *T–S–C* relative stereochemistry. Removal of the benzyl protective group and oxidation of the resulting alcohol (5) gave the ketone (1). This ketone, which is expected to have the same relative stereochemistry as

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