Related literature. The synthesis of anthracycline antibiotics (Arcamone, 1981) is of great interest since they are important anticancer drugs. The 1,4-dipolar-aryne reaction is very useful for the preparation of tetracyclic intermediates (Khanapure & Biehl, 1990) in the synthesis of anthracyclinones (Krohn, 1986). One of the important factors involved in this strategy is the control of regiochemistry in the aryne reaction. The title compound is one of the intermediates involved in the anthracyclinone synthesis.

This work was supported by the Robert A. Welch Foundation under grant N-118.

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Acta Cryst. (1990). C**46**, 926–928

Structure of a Pentacyclic Cage Enone

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(*Received* 14 *June* 1989; *accepted* 6 *December* 1989)

Abstract. 8-Methylene-1-phenylpentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-11-one (2*a*), $C_{18}H_{16}O$, $M_r = 248{\cdot}35$, monoclinic, $P2_1/n$, $a = 10{\cdot}359$ (2), $b = 6{\cdot}579$ (1), $c = 19{\cdot}553$ (3) Å, $\beta = 102{\cdot}78$ (1)°, $V = 1299{\cdot}9$ (3) Å^3, $Z = 4$, $D_x = 1{\cdot}270$ g cm,$^{-3}$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71973$ Å, $\mu = 0{\cdot}80$ cm^{-1}, $F(000) = 528$, $T = 295$ K, $R = 0{\cdot}0587$ for 1967 reflections. Compound (2*a*) is a strained open-ended cage compound composed of four fused five-membered rings in envelope conformations and a planar four-membered ring. The molecule contains an exocyclic methylene and a ketone moiety. The two cross bonds in a 1–3 relationship to the methylene and ketone π systems are elongated to 1·587 (7) and 1·595 (3) Å which is consistent with a postulated through bond coupling in similar molecules. The ketone and methylene systems with attached atoms are each planar with an interplanar angle of 65·0 (2)°.

Experimental. As part of a program that is concerned with the synthesis and chemistry of novel polycyclic cage compounds (Marchand, 1989), the Wittig reaction of 1-phenylpentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione (1) (Marchand, Annapurna, Reddy, Watson & Nagl, 1989) with $Ph_3P{=\!=}CH_2$ has been studied (see scheme 1). This reaction potentially can afford the two cage enones (2*a*) and (2*b*); however, only (2*a*) was isolated (48% yield). A colorless crystal of dimensions $0{\cdot}65 \times 0{\cdot}20 \times 0{\cdot}15$ mm was mounted on a Nicolet $R3m/\mu$ update of a $P2_1$ diffractometer; data collected in the ω mode ($3 \leq 2\theta \leq 55°$) using a variable scan rate (4–29·3° min^{-1}); graphite-monochromated Mo $K\alpha$ radiation; lattice parameters from a least-squares refinement of 25 reflections ($22{\cdot}38 \leq 2\theta \leq 27{\cdot}63°$), angles measured by a centering routine, systematic absences ($h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$) consistent with space group $P2_1/n$; monitored reflections $\bar{3}21$ and $22\bar{3}$ showed variations of less than ±2%; 3405 reflections collected ($-13 \leq h \leq 13$, $0 \leq k \leq 8$, $0 \leq l \leq 25$), 2988 unique ($R_{\text{int}} = 0{\cdot}009$), equivalent reflections averaged, 1967 with $I \geq 3\sigma(I)$; Lorentz–polarization corrections applied, ψ-scan empirical absorption correction (transmission factors 0·960–0·921); structure solved by direct methods, block-cascade least-squares refinement, H atoms located in difference map and refined with isotropic thermal parameters; final $R = 0{\cdot}0587$, $wR = 0{\cdot}0520$ ($R = 0{\cdot}0908$ and $wR = 0{\cdot}0550$

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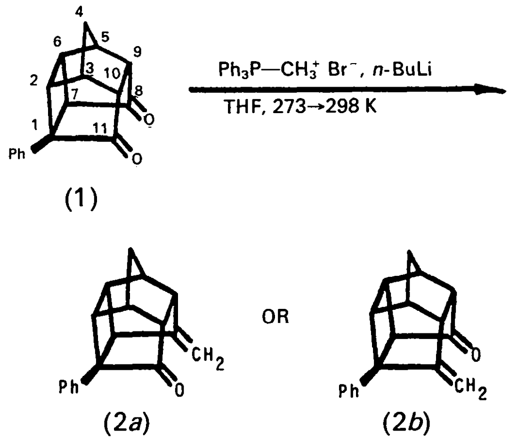

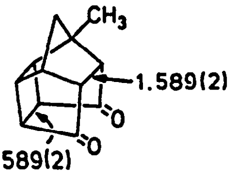

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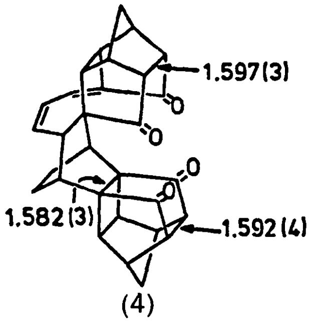

(4)

for all reflections) for 237 parameters and 1967 reflections, $S = 1{\cdot}564$, $(\Delta/\sigma)_{\max} = 0{\cdot}029$; largest peaks in the final difference map of 0·22 and $-0{\cdot}18$ e Å^{-3}; $\sum w(|F_o| - |F_c|)^2$ minimized with $w = [\sigma^2(F_o) + 0{\cdot}00024F_o^2]^{-1}$; isotropic extinction correction $F = F_c/[1 + 0{\cdot}002xF_c^2/\sin(2\theta)]^{0{\cdot}25}$ applied with x refined to 0·0023 (2). All computer programs supplied by Nicolet for Desktop 30 Microeclipse and Nova 4/C configuration (Nicolet Instrument Corporation, 1986); atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). Table 1 lists atomic positional parameters and Table 2 interatomic distances and valence angles.* Fig. 1 shows a thermal-ellipsoid plot of the molecule with the atomic numbering scheme.

Table 1. *Atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters* (Å$^2 \times 10^3$) *for* (2*a*)

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U
C(1)	1378 (2)	6334 (3)	6075 (1)	37 (1)
C(2)	1644 (2)	8396 (3)	5747 (1)	49 (1)
C(3)	2108 (2)	7959 (4)	5063 (1)	55 (1)
C(4)	3357 (2)	9239 (4)	5149 (1)	66 (1)
C(5)	4009 (2)	8358 (3)	5853 (1)	55 (1)
C(6)	2960 (2)	8650 (3)	6291 (1)	53 (1)
C(7)	2759 (2)	6567 (3)	6623 (1)	46 (1)
C(8)	3795 (2)	5227 (3)	6443 (1)	48 (1)
C(9)	3949 (2)	6046 (3)	5753 (1)	50 (1)
C(10)	2603 (2)	5780 (3)	5186 (1)	49 (1)
C(11)	1604 (2)	4802 (3)	5534 (1)	39 (1)
O(11)	1085 (1)	3171 (2)	5408 (1)	53 (1)
C(12)	198 (2)	5965 (3)	6380 (1)	42 (1)
C(13)	−838 (2)	7323 (4)	6307 (1)	55 (1)
C(14)	−1914 (2)	6890 (4)	6605 (1)	70 (1)
C(15)	−1953 (3)	5147 (5)	6966 (1)	79 (1)
C(16)	−936 (3)	3800 (4)	7047 (1)	78 (1)
C(17)	132 (2)	4202 (4)	6754 (1)	60 (1)
C(18)	4442 (3)	3711 (4)	6810 (2)	69 (1)

Table 2. *Bond lengths* (Å) *and angles* (°) *for compound* (2*a*)

C(1)—C(2)	1·551 (3)	C(1)—C(7)	1·595 (2)
C(1)—C(11)	1·517 (3)	C(1)—C(12)	1·494 (3)
C(2)—C(3)	1·545 (4)	C(2)—C(6)	1·542 (3)
C(3)—C(4)	1·522 (3)	C(3)—C(10)	1·523 (3)
C(4)—C(5)	1·509 (3)	C(5)—C(6)	1·538 (3)
C(5)—C(9)	1·533 (3)	C(6)—C(7)	1·550 (3)
C(7)—C(8)	1·490 (3)	C(8)—C(9)	1·495 (3)
C(8)—C(18)	1·321 (3)	C(9)—C(10)	1·587 (3)
C(10)—C(11)	1·502 (3)	C(11)—O(11)	1·201 (2)
C(12)—C(13)	1·379 (3)	C(12)—C(17)	1·381 (3)
C(13)—C(14)	1·397 (3)	C(14)—C(15)	1·352 (4)
C(15)—C(16)	1·358 (4)	C(16)—C(17)	1·380 (4)
C(2)—C(1)—C(7)	88·8 (1)	C(2)—C(1)—C(11)	102·9 (2)
C(7)—C(1)—C(11)	106·2 (1)	C(2)—C(1)—C(12)	122·9 (2)
C(7)—C(1)—C(12)	116·0 (2)	C(11)—C(1)—C(12)	115·9 (2)
C(1)—C(2)—C(3)	108·2 (2)	C(1)—C(2)—C(6)	91·2 (1)
C(3)—C(2)—C(6)	102·8 (2)	C(2)—C(3)—C(4)	102·8 (2)
C(2)—C(3)—C(10)	101·3 (2)	C(4)—C(3)—C(10)	104·8 (2)
C(3)—C(4)—C(5)	94·9 (2)	C(4)—C(5)—C(6)	103·4 (2)
C(4)—C(5)—C(9)	105·5 (2)	C(6)—C(5)—C(9)	100·4 (2)
C(2)—C(6)—C(5)	103·1 (2)	C(2)—C(6)—C(7)	90·8 (2)
C(5)—C(6)—C(7)	107·5 (2)	C(1)—C(7)—C(6)	89·3 (1)
C(1)—C(7)—C(8)	111·7 (2)	C(6)—C(7)—C(8)	104·7 (2)
C(7)—C(8)—C(9)	103·1 (2)	C(7)—C(8)—C(18)	128·6 (2)
C(9)—C(8)—C(18)	128·3 (2)	C(5)—C(9)—C(8)	104·6 (2)
C(5)—C(9)—C(10)	101·7 (2)	C(8)—C(9)—C(10)	109·7 (2)
C(3)—C(10)—C(9)	102·7 (2)	C(3)—C(10)—C(11)	103·5 (2)
C(9)—C(10)—C(11)	108·6 (2)	C(1)—C(11)—C(10)	105·0 (2)
C(1)—C(11)—O(11)	127·2 (2)	C(10)—C(11)—O(11)	127·8 (2)
C(1)—C(12)—C(13)	122·7 (2)	C(1)—C(12)—C(17)	119·3 (2)
C(13)—C(12)—C(17)	118·1 (2)	C(12)—C(13)—C(14)	119·9 (2)
C(13)—C(14)—C(15)	120·6 (2)	C(14)—C(15)—C(16)	120·2 (3)
C(15)—C(16)—C(17)	119·9 (3)	C(12)—C(17)—C(16)	121·3 (2)

Related literature. The X-ray structures of (3) (Marchand, Suri, Earlywine, Powell & van der Helm, 1984) and (4) (Mehta, Singh, Srikrishna, Cameron & Chan, 1979) have been reported. Calculated (MM2, MNDO, STO-3G) bond lengths in substituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecanediones have been published (Ōsawa & Kanematsu, 1986; Marchand, Huang, Kaya, Baker, Jemmis & Dixon, 1987), and the bond elongation has been discussed in these papers and for related structures (Watson, Nagl, Marchand, Reddy & Reddy, 1989). The use of these materials in synthesizing polycyclic cage structures (Marchand, 1989) and polycyclopentanoid natural

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* Lists of H-atom coordinates, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52519 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

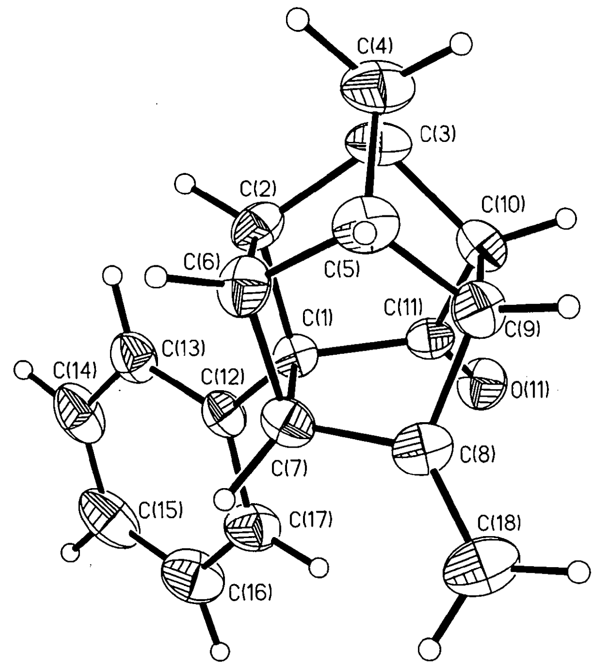

Fig. 1. Compound (2*a*) with thermal ellipsoids at the 30% probability level. H atoms are shown as spheres of arbitrary size.

products (Mehta, Srikrishna, Reddy & Nair, 1981) have been discussed.

We thank the Robert A. Welch Foundation (Grant P-074 to WHW, B-963 to APM), the Air Force Office of Scientific Research (Grant AFOSR-88-0132 to APM) and the Texas Christian University and University of North Texas Faculty Research Committees for financial support of this study.

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Acta Cryst. (1990). C**46**, 928–931

Structure of 1,7,10,16-Tetraoxa-4,13-dithiacyclooctadecane-2,6-dione at 163 K

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(*Received* 11 *September* 1989; *accepted* 14 *November* 1989)

Abstract. $C_{12}H_{20}O_6S_2$, $M_r = 324{\cdot}41$, triclinic, $P\bar{1}$, $a = 8{\cdot}7876\,(13)$, $b = 8{\cdot}6117\,(12)$, $c = 11{\cdot}855\,(2)$ Å, $\alpha = 90{\cdot}391\,(12)$, $\beta = 118{\cdot}85\,(2)$, $\gamma = 97{\cdot}823\,(10)°$, $V = 775{\cdot}8\,(2)$ Å^3, $Z = 2$, $D_x = 1{\cdot}389$ g cm^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0{\cdot}71069$ Å, $\mu = 3{\cdot}476$ cm^{-1}, $F(000) = 344$, $R = 0{\cdot}0407$ for 2274 reflections ($F \geq 4\sigma_F$). The macrocycle backbone forms an elliptical cavity with approximate $C2$ symmetry despite the presence of the carbonyl groups. The conformation, beginning at O1, is $(ag^-g^+,\ g^+aa,\ ag^+a)_2$; all C—S—C—C fragments are *gauche* whereas all C—O—C—C fragments are *anti*. Differences in torsion angles related by the pseudo-twofold axis are less than 17° (r.m.s. deviation: 9·5°). The macrocycle is not planar; the S atoms are 1·1702 (7) and 1·1289 (7) Å out of the mean plane of the 18 backbone atoms and pointed out of the cavity [the dihedral angles between the C—S—C fragments and the backbone mean plane are 114·43 (11) and 115·91 (13)°]. Two H atoms are inside the cavity. The carbonyl O atoms are 0·184 (2) and 0·847 (2) Å out of the plane. The average C—C, C—O(ether) and C—S bond distances are 1·504 (16), 1·424 (8) and 1·814 (11) Å. Bonds in the ester portions are also normal.

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0108-2701/90/050928-04$03.00