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VEGA, R., LÓPEZ-CASTRO, A. & MÁRQUEZ, R. (1983). *Acta Cryst.* C39, 464–466.

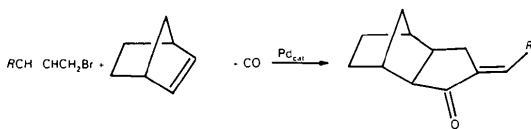# 4-Oxatetracyclo[9.2.1.0²,¹⁰.0³,⁸]tetradec-3(8)-ene-5-spiro-4′-tricyclo[5.2.1.0²′,⁶′]decan-3′-one, C₂₂H₂₈O₂

BY GABRIELE BOCELLI

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Abstract. $M_r = 324.46$, monoclinic, $P2_1/c$, $a = 13.410\,(2)$, $b = 10.840\,(2)$, $c = 12.444\,(3)$ Å, $\beta = 98.42\,(4)°$, $Z = 4$, $V = 1789.4\,(6)$ Å³, $D_x = 1.20$ g cm⁻³, Ni-filtered Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å, $\mu = 5.49$ cm⁻¹, $F(000) = 704$, room temperature, $R = 0.060$, 1822 observed reflections. The six-membered ring shows a conformation near to a half chair, while the five-membered rings have envelope conformations. Ring distances C(1)–O(1) [1.381 (4) Å] and C(13)–O(1) [1.459 (4) Å] indicate some conjugation with the double bond, even though this bond [C(1)–C(10) 1.329 (5) Å] is not longer than normal.

Introduction. Sequential olefin and carbon monoxide insertion into a Pd–C bond, obtained from oxidative addition of allylic bromides $RCH=CHCH_2Br$ to Pd⁰ complexes, leads to five-carbon-atom ring closure followed by hydrogen elimination. In this way a catalytic reaction can be achieved according to the following scheme (Amari, Catellani & Chiusoli, 1984):

When $R = H$, however, the product is found in the form of a spirocyclic dimer, which easily crystallizes from 95% ethanol, m.p. 362–363 K.

Its structure was deemed worth studying because of the high degree of regio- and stereoselectivity of the reaction.

Experimental. D_m not determined. Colourless prism $0.11 \times 0.15 \times 0.62$ mm. Siemens AED single-crystal

diffractometer; General Automation Jumbo 220 computer. Cell parameters by least-squares fit of 23 automatically centred reflections ($15.4 \leq \theta \leq 48.9°$). Intensity data with a modified version (Belletti, Ugozzoli, Cantoni & Pasquinelli, 1979) of the Lehmann & Larsen (1974) procedure. One check reflection every 50 counts, no significant decay. $2\theta_{max} = 140°$. $-16 \leq h \leq 16$, $0 \leq k \leq 13$, $0 \leq l \leq 15$. 3616 reflections collected, 3464 unique, $R_{int} = 0.0114$, 1822 observed at $2\sigma(I)$ level. Direct methods with *SHELX*76 (Sheldrick, 1976) which was employed throughout the refinement procedure. H atoms (from ΔF map) isotropic, rest anisotropic, block-matrix least squares, $\sum w(\Delta F)^2$ minimized, $R = 0.060$, $R_w = 0.064$,* $w = 1.0/(\sigma^2 F + 0.001745F^2)$, 130 and 200 parameters refined in the last cycles. $\Delta\rho_{max}$ 0.29 e Å⁻³. $(\Delta/\sigma)_{max}$ 0.76. Scattering factors of *SHELX*76. All calculations performed on a Gould SEL 32/77 computer.

Discussion. Atomic parameters are given in Table 1, bond distances and angles in Table 2. A drawing of the molecule is given in Fig. 1.

The structure of the compound, suggested by its elemental analysis and spectral data, is confirmed by X-ray analysis.

The six-membered ring adopts a conformation which is near to a half chair, leaving the C(12) out-of-plane of the remaining atoms of the ring by 0.66 (5) Å [0.16 (1) Å is the maximum out-of-plane distance for the five atoms of the ring plane]. This ring is rotated by 72.2 (2)° with respect to the spiro ring plane.

All the five-membered rings of the molecule exhibit envelope conformations. Following the Cremer & Pople (1975) notation the maximum deviations from the theoretical φ puckering parameter range from 0·2 (2) to 1·6 (3)°. Only that fused to the six-membered ring shows a greater value of 6·3 (9)°. The Q parameter for this ring is 0·014 (4) Å while it is in the range

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and* B_{eq} *values (according to Hamilton, 1959)*

	x	y	z	$B_{eq}(\text{Å}^2)$
O(1)	8204 (2)	493 (2)	−729 (2)	4·19
O(2)	8219 (3)	−2185 (4)	−1766 (4)	10·57
C(1)	8611 (3)	1226 (3)	133 (3)	3·66
C(2)	8716 (3)	2570 (3)	−63 (3)	3·69
C(3)	7728 (3)	3294 (4)	−356 (4)	4·63
C(4)	7992 (5)	4634 (4)	−556 (5)	6·36
C(5)	8394 (5)	5129 (4)	601 (4)	6·72
C(6)	8331 (4)	3982 (4)	1321 (4)	5·40
C(7)	7362 (4)	3363 (4)	749 (4)	5·76
C(8)	9136 (3)	3068 (4)	1108 (3)	4·41
C(9)	9245 (4)	1937 (4)	1873 (3)	4·98
C(10)	8901 (3)	858 (4)	1149 (3)	4·51
C(11)	8898 (4)	−475 (4)	1485 (4)	5·93
C(12)	8721 (4)	−1273 (4)	451 (4)	5·78
C(13)	7900 (3)	−724 (3)	−396 (4)	4·39
C(14)	7691 (3)	−1428 (3)	−1460 (3)	5·07
C(15)	6662 (3)	−1072 (4)	−2046 (3)	4·74
C(16)	6095 (3)	−529 (3)	−1145 (3)	4·32
C(17)	6847 (3)	−617 (4)	−88 (3)	4·73
C(18)	5978 (4)	−2142 (4)	−2505 (4)	6·25
C(19)	5583 (4)	−2594 (4)	−1482 (4)	6·05
C(20)	5159 (3)	−1347 (4)	−1220 (4)	5·09
C(21)	4453 (4)	−1046 (5)	−2260 (4)	6·59
C(22)	5012 (4)	−1591 (6)	−3155 (5)	7·46

Table 2. *Bond distances* (Å) *and angles* (°)

O(1)–C(1)	1·381 (4)	C(5)–C(6)	1·542 (7)	C(14)–C(15)	1·513 (5)
O(1)–C(13)	1·459 (4)	C(6)–C(7)	1·541 (7)	C(15)–C(16)	1·559 (6)
O(2)–C(14)	1·183 (6)	C(6)–C(8)	1·517 (7)	C(15)–C(18)	1·536 (6)
C(1)–C(2)	1·487 (5)	C(8)–C(9)	1·546 (6)	C(16)–C(17)	1·539 (5)
C(1)–C(10)	1·329 (5)	C(9)–C(10)	1·507 (6)	C(16)–C(20)	1·528 (6)
C(2)–C(3)	1·537 (6)	C(10)–C(11)	1·504 (6)	C(18)–C(19)	1·529 (7)
C(2)–C(8)	1·579 (5)	C(11)–C(12)	1·540 (7)	C(18)–C(22)	1·543 (7)
C(3)–C(4)	1·534 (6)	C(12)–C(13)	1·529 (6)	C(19)–C(20)	1·520 (6)
C(3)–C(7)	1·528 (7)	C(13)–C(14)	1·518 (5)	C(20)–C(21)	1·523 (7)
C(4)–C(5)	1·557 (8)	C(13)–C(17)	1·521 (6)	C(21)–C(22)	1·548 (8)

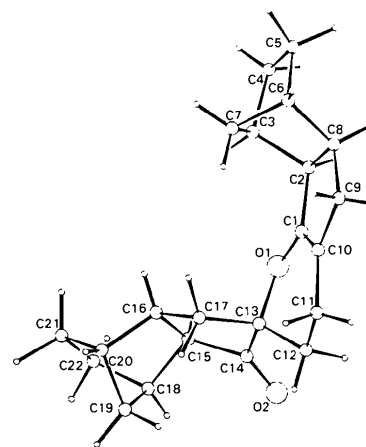|			
C(1)–O(1)–C(13)	113·3 (3)	O(1)–C(13)–C(12)	110·2 (3)
O(1)–C(1)–C(10)	126·4 (3)	C(12)–C(13)–C(17)	117·2 (3)
O(1)–C(1)–C(2)	118·2 (3)	C(12)–C(13)–C(14)	115·3 (3)
C(2)–C(1)–C(10)	115·4 (3)	O(1)–C(13)–C(17)	108·1 (3)
C(1)–C(2)–C(8)	102·3 (3)	O(1)–C(13)–C(14)	103·3 (3)
C(1)–C(2)–C(3)	116·1 (3)	C(14)–C(13)–C(17)	101·5 (3)
C(3)–C(2)–C(8)	102·9 (3)	O(2)–C(14)–C(13)	125·9 (4)
C(2)–C(3)–C(7)	101·0 (3)	C(13)–C(14)–C(15)	109·3 (3)
C(2)–C(3)–C(4)	108·2 (4)	O(2)–C(14)–C(15)	124·6 (4)
C(4)–C(3)–C(7)	102·3 (4)	C(14)–C(15)–C(18)	116·1 (3)
C(3)–C(4)–C(5)	103·6 (4)	C(14)–C(15)–C(16)	104·8 (3)
C(4)–C(5)–C(6)	102·6 (4)	C(16)–C(15)–C(18)	103·0 (3)
C(5)–C(6)–C(8)	108·9 (4)	C(15)–C(16)–C(20)	102·7 (3)
C(5)–C(6)–C(7)	101·4 (4)	C(15)–C(16)–C(17)	105·3 (3)
C(7)–C(6)–C(8)	102·0 (4)	C(17)–C(16)–C(20)	116·5 (3)
C(3)–C(7)–C(6)	94·4 (4)	C(13)–C(17)–C(16)	107·8 (3)
C(2)–C(8)–C(6)	102·6 (3)	C(15)–C(18)–C(22)	108·2 (4)
C(6)–C(8)–C(9)	114·6 (4)	C(15)–C(18)–C(19)	101·1 (4)
C(2)–C(8)–C(9)	106·6 (3)	C(19)–C(18)–C(22)	101·2 (4)
C(8)–C(9)–C(10)	104·7 (3)	C(18)–C(19)–C(20)	94·6 (4)
C(1)–C(10)–C(9)	110·9 (3)	C(16)–C(20)–C(19)	101·5 (4)
C(9)–C(10)–C(11)	126·3 (4)	C(19)–C(20)–C(21)	102·3 (4)
C(1)–C(10)–C(11)	122·7 (4)	C(16)–C(20)–C(21)	109·3 (4)
C(10)–C(11)–C(12)	108·3 (4)	C(20)–C(21)–C(22)	102·9 (4)
C(11)–C(12)–C(13)	111·4 (4)	C(18)–C(22)–C(21)	103·2 (4)

Fig. 1. A view of the molecule down **c**.

0·33 (10)–0·59 (5) Å for the remaining five-membered rings. The distortion of the fused five-membered ring is probably due to the sp^2 hybridization of C(1) and C(10).

The C(1)–C(10) distance of 1·329 (5) Å is normal for a double bond and the interplanar angle of 2·4 (2)° between C(2), C(1), C(10), C(9) and O(1), C(1), C(10), C(11) is consistent with the planarity expected for such a bond. The fact that the O(1)–C(1) length [1·381 (4) Å] is shorter than O(1)–C(13) [1·459 (4) Å] indicates a certain degree of conjugation with the C(1)–C(10) double bond [1·329 (5) Å] even though the latter is not longer than the standard C=C bond length (1·335 Å).

As always observed in norbornane derivatives the endocyclic angles at C(7) and C(19) are noticeably smaller [94·4 (4), 94·6 (4)°] than the others of the groups.

Only the H(7)$\cdots$H(21)($-x+1$, $-y$, $-z$) distance of 2·15 (7) Å is considerably shorter than the sum of the van der Waals radii; the remaining intermolecular contacts are in the range of van der Waals interactions.

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