Structural Studies of Dihalocarbene Adducts with (−)-R-Carvone. II. Structure and Absolute Configuration of (1R,2R,4R)-7,7-Dibromo-4-isopropenyl-1-methylbicyclo-[4.1.0]heptan-2-ol

By E. E. Castellano and J. Zukerman-Schpector*

Instituto de Física e Química de São Carlos, Universidade de São Paulo, Caixa Postal 369, 13.560 – São Carlos, São Paulo, Brazil

and Timothy J. Brocksom and Elisabete T. Canevarolo

Departamento de Química, Universidade Federal de São Carlos, Caixa Postal 676, 13.560 – São Carlos, São Paulo, Brazil

Abstract. $C_{11}H_{16}Br_2O$, $M_r = 324.07$, monoclinic, $P2_1$, $a = 13.935$ (2), $b = 6.380$ (1), $c = 14.701$ (2) Å, $\beta = 110.062$ (9)°, $V = 1227.7$ (6) Å^3, $Z = 4$, $D_x = 1.75$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 6.4$ mm^{-1}, $F(000) = 640$, $T = 296$ K, $R = 0.068$ for 1464 observed reflections. The two independent molecules in the asymmetric unit are essentially identical. They are hydrogen bonded to each other in a fashion giving rise to an infinite helical configuration of hydrogen bonds around the symmetry axis $|O(1)\cdots O(1') = 2.79$ (2), 2.80 (2) Å; $O(1)-H(O1)\cdots O(1') = 146$ (1), 159 (1)°|. The absolute configuration of the molecule was ascertained both by chemical means and by a comparison of R values for the determined structure and its inverted structure.

Introduction. The cycloaddition of dichlorocarbene to (−)-R-carvone (I) gives the bis-adducts (II), as determined by X-ray diffraction methods (Zukerman-Schpector, Castellano, Oliva, Brocksom & Canevarolo, 1984). Thus the addition is not chemoselective with respect to the two chemically different double bonds, nor is it stereoselective with respect to the Δ^8 double bond. The analogous reaction of dibromocarbene with (−)-R-carvone (I) is quite different in that it leads chemoselectively to the mono-adduct (III) in extremely high yields (Sydnes & Skattebøl, 1975; Brocksom, Canevarolo & Lopes, 1985). This reaction is mechanistically more informative, as the product (III) must demonstrate the true stereochemical course of this cycloaddition. The mono-dibromocarbene adduct (III) was obtained in over 80% yield and purified by conventional chromatographic methods (on attempted vacuum distillation the product decomposed rather violently when the oil-bath temperature reached about

423 K) to give light-brown needles with a very low melting point (313–319 K) unsuitable for X-ray studies. Therefore, we prepared the corresponding alcohol by lithium aluminium hydride reduction of (III). The alcohol formed as an epimeric mixture was surprisingly difficult to separate by preparative thick-plate chromatography. ^{1}H NMR analysis led to the conclusion that both epimers adopt conformations where the alcohol group is equatorial. This explains the chromatographic behaviour but creates a new stereochemical problem as to the relative configurations of the two alcohols. After exhaustive preparative thick-plate chromatography we were able to obtain both epimers in a pure state, and one isomer (IV) crystallized allowing us to perform a three-dimensional crystal-structure analysis.

(IIa) R$_1$=Cl, R$_2$=H
(IIb) R$_1$=H, R$_2$=Cl
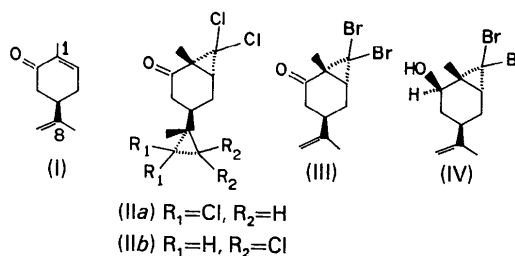
Experimental. Prismatic yellow crystals, $0.30 \times 0.10 \times 0.10$ mm; Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$; cell parameters by least squares on setting angles for 25 reflections, $18 < 2\theta < 40°$; ω–2θ scans, scan speed $6.7°$ min^{-1} max., range of hkl: $h < 15$, $k < 7$, $-16 < l < 16$; standards $\bar{1}07$, 040, varied $\pm 1.8\%$ of mean intensities over data collection; 1970 reflections measured, $2\theta_{max} = 45°$, 1890 unique, $R_{int} = 0.040$, 1466 observed above $2\sigma(I)$; Lp and absorption corrections (transmission factors 0.61–0.49); structure solved

* Present address: Departamento de Química/CCEN, Universidade Federal de Alagoas, 57.000 – Maceió, Alagoas, Brazil.

by direct methods, H atoms located in a difference map; block least-squares refinement minimizing $\sum w(|F_o|-|F_c|)^2$ with $w = [\sigma^2(F_o) + 0\cdot00037F_o^2]^{-1}$, 253 parameters refined: coordinates and anisotropic thermal parameters for non-H atoms; H atoms at fixed positions ($B = 6\cdot0$ Å² for methyl H and $4\cdot0$ Å² for the rest); excluding unobserved and two reflections ($100,\overline{4}24$) $R = 0\cdot068$, $wR = 0\cdot053$, $R_G = 0\cdot058$; max. $\Delta/\sigma = 0\cdot005$, $\Delta\rho$ excursions within $-0\cdot42$ and $0\cdot54$ e Å⁻³; scattering factors for non-H atoms from Cromer & Mann (1968) with corrections for anomalous dispersion from Cromer & Liberman (1970), for H from Stewart, Davidson & Simpson (1965); programs used: *MULTAN*80 (Main *et al.*, 1980), *SHELX*76 (Sheldrick, 1976) and *ORTEP* (Johnson, 1965).

Discussion. Fig. 1 is a stereoscopic projection of the unit-cell contents down the unique axis. Positional parameters and the equivalent values of the anisotropic temperature factors are given in Table 1.* Bond lengths and angles are given in Table 2. There are two independent molecules in the asymmetric unit which are essentially identical: in fact a least-squares fit (Kabsch, 1976) gives a mean deviation between equivalent atoms of $0\cdot08$ Å. The absolute configuration of the molecule was determined following Hamilton (1965) and by chemical means, *viz* derivation from the natural product $(-)$-R-carvone (I). The corresponding R values obtained by refinement of the inverted structure are $R = 0\cdot069$, $wR = 0\cdot057$, $R_G = 0\cdot061$. Applying the R-factor-ratio test, we obtain $\mathscr{R} = 1\cdot052$, much greater than the value $\mathscr{R}_{1,1211,0.005} = 1\cdot003$ interpolated from the Hamilton tables for the $0\cdot005$

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42540 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
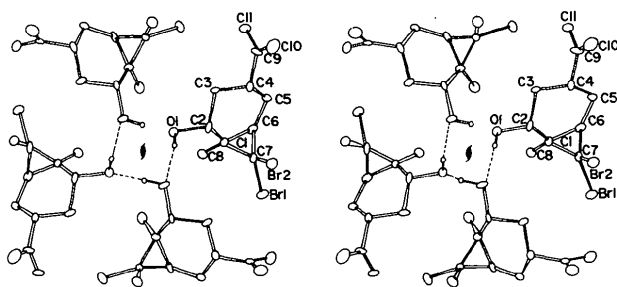

Fig. 1. Projection of the unit-cell contents along the unique axis.

Table 1. *Atomic coordinates and calculated isotropic temperature factors with e.s.d.'s in parentheses*

	x	y	z	B_{iso}*(Å²)
Br(1)	−0·1762 (2)	0·0521 (5)	−0·6356 (1)	4·46 (8)
Br(2)	−0·1189 (2)	−0·3851 (4)	−0·5343 (1)	4·02 (7)
O(1)	−0·3800 (8)	−0·234 (2)	−0·4392 (8)	2·9 (4)
C(1)	−0·239 (1)	−0·066 (3)	−0·466 (1)	2·6 (6)
C(2)	−0·273 (1)	−0·244 (3)	−0·419 (1)	2·4 (6)
C(3)	−0·215 (1)	−0·240 (4)	−0·310 (1)	3·5 (6)
C(4)	−0·100 (1)	−0·280 (4)	−0·293 (1)	3·5 (7)
C(5)	−0·053 (1)	−0·106 (4)	−0·330 (1)	3·5 (7)
C(6)	−0·128 (1)	0·001 (3)	−0·424 (1)	2·7 (6)
C(7)	−0·165 (1)	−0·111 (4)	−0·518 (1)	3·8 (7)
C(8)	−0·315 (1)	0·113 (4)	−0·503 (1)	3·8 (7)
C(9)	−0·040 (2)	−0·342 (4)	−0·187 (2)	4·2 (8)
C(10)	0·012 (2)	−0·518 (6)	−0·172 (2)	8· (1)
C(11)	−0·045 (2)	−0·188 (5)	−0·113 (1)	6· (1)
Br(1')	−0·7707 (1)	−0·1967 (1)	−0·8990 (2)	4·62 (8)
Br(2')	−0·6775 (2)	−0·6423 (4)	−0·9065 (1)	3·92 (7)
O(1')	−0·4808 (8)	−0·471 (2)	−0·6041 (7)	3·4 (4)
C(1')	−0·561 (1)	−0·307 (3)	−0·766 (1)	2·6 (6)
C(2')	−0·496 (1)	−0·486 (3)	−0·707 (1)	2·9 (6)
C(3')	−0·393 (1)	−0·488 (4)	−0·721 (1)	3·3 (6)
C(4')	−0·409 (1)	−0·545 (3)	−0·827 (1)	3·5 (7)
C(5')	−0·471 (1)	−0·359 (3)	−0·894 (1)	3·1 (6)
C(6')	−0·552 (1)	−0·262 (3)	−0·863 (1)	3·2 (6)
C(7')	−0·646 (1)	−0·356 (4)	−0·863 (1)	3·2 (6)
C(8')	−0·577 (1)	−0·130 (4)	0·709 (1)	4·0 (7)
C(9')	−0·310 (2)	−0·592 (4)	−0·845 (1)	2·9 (7)
C(10')	−0·294 (2)	−0·779 (4)	−0·871 (2)	5·4 (9)
C(11')	−0·234 (2)	−0·426 (4)	−0·829 (1)	5·2 (8)

* $B_{iso} = \frac{4}{3}\sum_i\sum_j T_{ij}B_{ij}$ (Hamilton, 1959).

Table 2. *Intramolecular bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Br(1)—C(7)	1·98 (2)	Br(1')—C(7')	1·92 (2)
Br(2)—C(7)	1·91 (2)	Br(2')—C(7')	1·93 (2)
O(1)—C(2)	1·42 (2)	O(1')—C(2')	1·46 (2)
C(1)—C(2)	1·49 (3)	C(1')—C(2')	1·53 (3)
C(1)—C(6)	1·52 (3)	C(1')—C(6')	1·50 (2)
C(1)—C(7)	1·51 (3)	C(1')—C(7')	1·54 (2)
C(1)—C(8)	1·53 (3)	C(1')—C(8')	1·47 (3)
C(2)—C(3)	1·53 (2)	C(2')—C(3')	1·52 (3)
C(3)—C(4)	1·56 (3)	C(3')—C(4')	1·54 (3)
C(4)—C(5)	1·48 (3)	C(4')—C(5')	1·59 (3)
C(4)—C(9)	1·55 (3)	C(4')—C(9')	1·52 (3)
C(5)—C(6)	1·57 (3)	C(5')—C(6')	1·49 (3)
C(6)—C(7)	1·48 (3)	C(6')—C(7')	1·44 (3)
C(9)—C(10)	1·31 (4)	C(9')—C(10')	1·30 (3)
C(9)—C(11)	1·49 (4)	C(9')—C(11')	1·46 (3)
C(2)—C(1)—C(6)	118· (1)	C(2')—C(1')—C(6')	117· (1)
C(2)—C(1)—C(7)	118· (1)	C(2')—C(1')—C(7')	119· (1)
C(2)—C(1)—C(8)	116· (1)	C(2')—C(1')—C(8')	115· (1)
C(6)—C(1)—C(7)	59· (1)	C(6')—C(1')—C(7')	57· (1)
C(6)—C(1)—C(8)	115· (1)	C(6')—C(1')—C(8')	118· (1)
C(7)—C(1)—C(8)	118· (1)	C(7')—C(1')—C(8')	118· (1)
O(1)—C(2)—C(1)	110· (1)	O(1')—C(2')—C(1')	113· (1)
O(1)—C(2)—C(3)	111· (1)	O(1')—C(2')—C(3')	110· (1)
C(1)—C(2)—C(3)	110· (1)	C(1')—C(2')—C(3')	109· (1)
C(2)—C(3)—C(4)	108· (1)	C(2')—C(3')—C(4')	109· (1)
C(3)—C(4)—C(5)	112· (1)	C(3')—C(4')—C(5')	108· (1)
C(3)—C(4)—C(9)	112· (1)	C(3')—C(4')—C(9')	113· (1)
C(5)—C(4)—C(9)	114· (1)	C(5')—C(4')—C(9')	112· (1)
C(4)—C(5)—C(6)	114· (1)	C(4')—C(5')—C(6')	115· (1)
C(1)—C(6)—C(5)	121· (1)	C(1')—C(6')—C(5')	122· (1)
C(1)—C(6)—C(7)	60· (1)	C(1')—C(6')—C(7')	63· (1)
C(5)—C(6)—C(7)	122· (1)	C(5')—C(6')—C(7')	128· (1)
Br(1)—C(7)—Br(2)	108· (1)	Br(1')—C(7')—Br(2')	109·1 (9)
Br(1)—C(7)—C(1)	119· (1)	Br(1')—C(7')—C(1')	119· (1)
Br(1)—C(7)—C(6)	117· (1)	Br(1')—C(7')—C(6')	121· (1)
Br(2)—C(7)—C(1)	124· (1)	Br(2')—C(7')—C(1')	121· (1)
Br(2)—C(7)—C(6)	122· (1)	Br(2')—C(7')—C(6')	120· (1)
C(1)—C(7)—C(6)	61· (1)	C(1')—C(7')—C(6')	60· (1)
C(4)—C(9)—C(10)	118· (1)	C(4')—C(9')—C(10')	119· (1)
C(4)—C(9)—C(11)	115· (1)	C(4')—C(9')—C(11')	119· (1)
C(10)—C(9)—C(11)	127· (1)	C(10')—C(9')—C(11')	122· (1)

significance level. Hence the hypothesis that the structure is described by the alternative enantiomorph was rejected at the 0·005 significance level. The main result of the present study is that the conformation of the alcohol is unambiguously determined to be that of (IV), as indicated in Fig. 1. Such information is an invaluable help in understanding the reaction mechanism involving this substance.

O(1) of one molecule is hydrogen bonded to O(1) of the other independent one, which in turn is hydrogen bonded to the O(1) related to the first one by the twofold screw axis, giving rise to an infinite helical arrangement of hydrogen bonds around the symmetry axis $|O(1)\cdots O(1') = 2\cdot79$ (2), $2\cdot80$ (2) Å; O(1)—H(O1) = 0·97 (2), 0·95 (2) Å; H(O1)$\cdots$O(1') = 1·94 (2), 1·89 (2) Å; O(1)—H(O1)$\cdots$O(1') = 146 (1), 159 (1)°|.

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Structure of N^2-(m-Chlorophenyl)-N^1,N^1-pentamethylenebenzamidine

BY E. TYKARSKA, M. JASKÓLSKI AND Z. KOSTURKIEWICZ*

Department of Crystallography, Faculty of Chemistry, A. Mickiewicz University, ul. Grunwaldzka 6, 60-780 Poznań, Poland

Abstract. 3-Chloro-N-(α-piperidinobenzylidene)aniline, $C_{18}H_{19}ClN_2$, $M_r = 298\cdot82$, orthorhombic, $P2_12_12_1$, $a = 10\cdot096$ (1), $b = 17\cdot128$ (2), $c = 9\cdot220$ (1) Å, $V = 1594\cdot4$ (3) Å^3, $Z = 4$, $D_m = 1\cdot25$, $D_x = 1\cdot24$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1\cdot57178$ Å, $\mu = 2\cdot06$ mm^{-1}, $F(000) = 632$, room temperature, $R = 0\cdot044$ for 1090 observed reflexions. The N=C(—C)—N amidine group is planar ($\chi^2 = 5\cdot02$). The C—N$_{\text{imine}}$ and C—N$_{\text{amine}}$ bond lengths are different, 1·290 (6) and 1·365 (6) Å, respectively. The phenyl ring is twisted by 60·2° and the m-chlorophenyl ring by 59·7° relative to the amidine plane, indicating there is no conjugation between the amidine and aromatic fragments.

Introduction. Compounds based on the amidine skeleton possess anaesthetic properties and are used in medicine for blocking nervous conduction. The title compound was synthetized and characterized by spectroscopic methods by Oszczapowicz, Raczyńska & Pawlik (1984). The present X-ray crystal structure analysis has been undertaken in order to reveal the details of the geometry of the benzamidine molecule. Our aim is to compare how the disposition of the side fragments relative to the central amidine group depends on the character and dimensions of those fragments. So far, no structural data have been reported for benzamidine derivatives. Benzamidines are based on a formamidine skeleton, $-N_I=C_FN_A<$, with the H atom substituted by a phenyl group. N$_{\text{imine}}$ and N$_{\text{amine}}$ are formally different. Nevertheless, X-ray and IR spectroscopic investigations of formamidines (Krajewski *et al.*, 1981) and acetamidines (Norrestam, Mertz & Crossland, 1983; Norrestam, 1984) show that the amidine group is planar with both nitrogen atoms having sp^2 hybridization. It is of interest to investigate the changes

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* To whom correspondence should be addressed.