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Novel Oxidative Rearrangement Product of the First *trans,cis,cis,cis*-[5.5.5.5]Fenestrane Derivative

PAUL A. WENDER,[a] MITCH A. DELONG[b] AND FRED C. WIREKO[b]

[a]*Department of Chemistry, Stanford University, Stanford, CA 94305, USA, and* [b]*The Procter and Gamble Company, Miami Valley Laboratories, PO Box 538707, Cincinnati, OH 452539-8707, USA. E-mail: wireko.fc@pg.com*

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Abstract

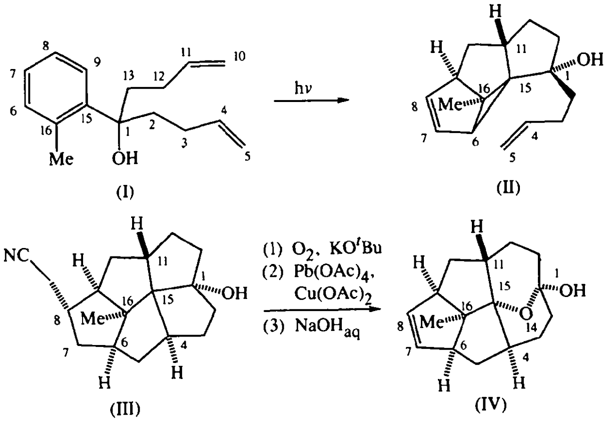
The structure of *rel*-(4*S*,6*R*,9*S*,11*S*)-1-hydroxy-16-methyl-14-oxapentacyclo[7.4.3.$0^{4,15}$.$0^{11,15}$.$0^{6,16}$]hexadeca-7-ene, $C_{16}H_{22}O_2$, (IV), has been determined. This study thus establishes compound (III), the precursor of (IV), as the first *trans,cis,cis,cis*-[5.5.5.5]fenestrane. The geometry around the central quaternary C atom of (IV) shows relatively little distortion. The C═C bond in the cyclopentene subunit is slightly shorter [1.305 (4) Å] than normal. Similarly, small departures from normal are seen in several C—C single bonds.

Comment

Fenestranes (Luef & Keese, 1993) are tetracycles sharing a central C atom. This connectivity feature gives rise to unique topologies along with the potential for severe strain. Several syntheses of the *cis,cis,cis,cis*-[5.5.5.5]fenestranes have been reported (Thommen, Gerber & Keese, 1991; Keese, Guidetti-Grept & Herzog, 1992). Prior to the current work, however, no synthesis of a *trans,cis,cis,cis*-[5.5.5.5]fenestrane system had been reported, despite impressive efforts toward this goal (Luyten & Keese, 1986). The strain of such fenestranes accounts in part for the difficulty associated with their synthesis as well as that encountered in the preparation of even the simpler *trans*-bicyclo[3.3.0]octanes. This strain and its manifestation in unusual geometries for carbon have also resulted in considerable theoretical interest in the fenestranes (Monkhorst, 1968; Hoffmann, Alder & Wilcott, 1970; Wiberg, Ellison & Wendoloski, 1976; Collins *et al.*, 1976; Kubiak, Fu, Gupta & Cook, 1990). Calculations on the fenestranes consistently predict a higher strain (*ca* 10 kcal mol^{-1}) for the *trans* isomer compared to the all-*cis* isomer (*e.g.* Kubiak, Fu, Gupta & Cook, 1990).

Recent studies on a novel variant of the arene–alkene photocycloaddition reaction have led to a successful synthesis of the first *trans,cis,cis,cis*-[5.5.5.5]fenestrane (Wender, Dove & deLong, 1996; deLong, 1992). In this synthesis, the arene–bisalkene (I), upon irradiation, gave the tetracycle (II). Earlier studies (Wender & Howbert, 1982, 1983; Wender & Singh, 1985, 1990; Wender & deLong, 1990) have shown that the vinyl cyclopropane subunit of these cycloadducts can be cleaved by free-radical addition to the vinyl group. In the current study, this cleavage involving the C6—C15 cyclopropane bond produces a radical at C15 which is trapped internally by the C4—C5 alkene. The resultant C5 radical then adds to the C6═C7 double bond to produce, after H-atom abstraction from the solvent, the fenestrane (III).

Compound (III) is not crystalline and its NMR spectrum lacks sufficient signal dispersion for complete assignment. Consequently, efforts were taken to convert (III) to a crystalline derivative in order to secure its structure by X-ray analysis. Oxidation of the acetonitrile group in (III) gave an acid which upon treatment with [$Pb(OAc)_4$] and [$Cu(OAc)_2$] and subsequent hydrolysis afforded crystalline fenestrane (IV). Compound (IV) results from a novel oxidative cleavage of a σ bond, assisted presumably by the strain of the fenestrane system. A full description of the synthesis is given elsewhere (deLong, 1992). The structure of (IV) is described herein. This determination establishes the structure of (III) as a *trans,cis,cis,cis*-[5.5.5.5]fenestrane. The power of this synthetic strategy rests in its capacity to produce novel fenestranes in only three steps from commercially available starting materials.



The H atoms at C4 and C11 in (IV) are in a *trans* relationship to each other, thus establishing the stereochemistry of this fenestrane derivative. There is some distortion in the molecule towards planar bonding as can be seen from the bond angles around the central C atom: C4—C15—C11 = 116.5 (2) and O14—C15—C16 = 111.9 (1)°. However, this strain is less than that ex-

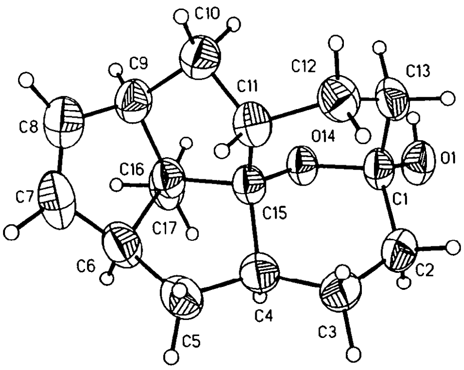


Fig. 1. The molecular structure of the fenestrane with atomic numbering. Displacement ellipsoids are plotted at the 50% probability level.

hibited by other fenestranes where deviations as large as 129.2 (5) and 128.3 (6)° in the [4.4.4.5]fenestrane series have been observed (Rao, George, Wolff & Agosta, 1985). [5.5.5.5]Fenestranes also show planar distortion (Guidetti-Grept *et al.*, 1995). The incorporation of two six-membered rings in (IV) minimizes this distortion. The C=C bond length in the cyclopentene subunit is slightly shorter [1.305 (4) Å] than normal. C6—C16 and C9—C16 are lengthened to 1.570 (3) and 1.557 (3) Å, respectively. Several bonds along the perimeter of the fenestrane exhibit some shortening. The molecules form hydrogen-bonded dimers about inversion centers (1 − *x*, −*y*, 1 − *z*) as shown (Fig. 2). The donor and acceptor O atoms, O1···O4^{i}, are separated by 2.858 (2) Å and subtend an angle of 167 (3)° at the H atom.

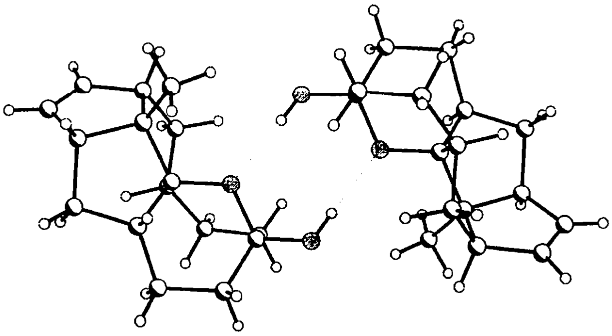


Fig. 2. The hydrogen bonding between two symmetry-related molecules.

Experimental

Crystals of (IV) were obtained by slow evaporation from diethyl ether solution.

Crystal data

$C_{16}H_{22}O_2$
$M_r = 246.34$
Monoclinic
$P2_1/c$
$a = 8.567\ (2)$ Å
$b = 12.189\ (2)$ Å
$c = 12.557\ (3)$ Å
$\beta = 98.05\ (3)°$
$V = 1298.3\ (5)$ Å^3
$Z = 4$
$D_x = 1.260$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54059$ Å
Cell parameters from 25 reflections
$\theta = 18–30°$
$\mu = 0.635$ mm^{-1}
$T = 293\ (2)$ K
Rectangular
0.40 × 0.35 × 0.3 mm
Colorless

Data collection

Rigaku AFC-5R RU200 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2183 measured reflections
2035 independent reflections
1871 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.021$
$\theta_{\rm max} = 61.86°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 13$
$l = -14 \rightarrow 14$
3 standard reflections every 150 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.126$
$S = 1.080$
2035 reflections
229 parameters
H-atom positions refined, *U* values fixed in final cycle

$w = 1/[\sigma^2(F_o^2) + (0.0573P)^2 + 0.4621P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.048$
$\Delta\rho_{\rm max} = 0.253$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.187$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

C1—O1	1.401 (2)	C11—C15	1.543 (3)
C1—O14	1.459 (2)	C15—O14	1.443 (2)
C4—C15	1.524 (3)	C15—C16	1.543 (2)
C7—C8	1.305 (4)		
O14—C15—C16	111.9 (1)	O14—C15—C11	110.6 (1)
O14—C15—C4	108.4 (2)	C16—C15—C11	104.7 (2)
C4—C15—C16	104.7 (1)	C4—C15—C11	116.5 (2)

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992*a*). Cell refinement: *TEXSAN* (Molcular Structure Corporation, 1992*b*). Data reduction: *TEXSAN*. Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXTL* (Sheldrick, 1994). Molecular graphics: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1026). Services for accessing these data are described at the back of the journal.

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1,3-Diphenyl-2-tricyclo[3.3.1.1^{3,7}]dec-2-ylidenepropane-1,3-diimine, and its -1-imino-3-one and -1,3-dione Derivatives

Ching-Fa Yao,* Yuh-Shih Chen, Wen-Chang Chen, Ren-Shyang Sheu, Jen-Kou Lai and Chuen-Her Ueng*

Department of Chemistry, National Taiwan Normal University 88, Sec. 4, Ding-Jou Road, Taipei 117, Taiwan

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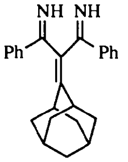
Abstract

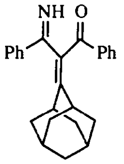
1,3-Diphenyl-2-tricyclo[3.3.1.1^{3,7}]dec-2-ylidenepropane-1,3-diimine, $C_{25}H_{26}N_2$, (1), 1-imino-1,3-diphenyl-2-tricyclo[3.3.1.1^{3,7}]dec-2-ylidenepropan-3-one, $C_{25}H_{25}NO$, (2) and 1,3-diphenyl-2-tricyclo[3.3.1.1^{3,7}]dec-2-ylidenepropane-1,3-dione, $C_{25}H_{24}O_2$, (3), were prepared from the reactions of 2-(dicyanomethylene)adamantane with phenylmagnesium bromide upon workup with dry methanol or dilute acid aqueous solution, and their crystal structures were determined by X-ray diffraction. Compounds (1) and (2) have similar molecular structures with the two imino groups in (1) and the imino and ketone groups in (2) being on the same side of the C1, C2, C12, C13 plane, compared with the two O atoms in compound (3), which are on opposite sides.

Comment

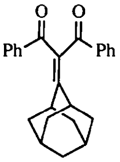
Michael addition reactions involve organometallic compounds with activated double bonds. Grignard reagents reacting with ylidenemononitriles always generate 1,4-addition or reductive products (Latif, Mishriky & Mohsen, 1974; Latif, Zeid & Assad, 1970). The nature of the resulting products depends on the organomagnesium halides as well as on the substrate, in particular on the stereochemical requirements of each (Latif, Girgis & Michael, 1970). Here, we report on the reactions of 2-(dicyanomethylene)adamantane with phenylmagnesium bromide which generate 1,2-addition products. The generation of different 1,2-products instead of 1,4-products or reductive products is ascribed to the steric effects between 2-(dicyanomethylene)adamantane and phenylmagnesium bromide.



(1)



(2)



(3)

The crystals of the title compounds, (1), (2) and (3), all have centrosymmetric monoclinic space groups and have similar cell volumes. However, compound (3) belongs to a *C*-centered rather than a primitive space group like those of (1) and (2). Compounds (1) and (2) have similar molecular structures with the two imino groups in (1) and the imino and ketone groups in (2) all on the same side of the C1, C2, C12, C13 plane around C1. There is a crystallographic twofold axis through C1, C2 and C6 in (3), and the two O atoms are on opposite sides of the C1, C2, C12, C13 plane. The C=NH bond length [1.243 (3) Å] in (2) is shorter than those in (1) [1.269 (5) and 1.279 (5) Å] and the C=O bond length [1.239 (3) Å] in (2) is longer than those in (3) [1.224 (3) Å]. Compounds (1) and (2) have intramolecular hydrogen bonding *via* N1···HN2 and O···HN contacts [N1···N2 3.308 (5), N1···HN2 2.554 (3) Å; N···O 3.100 (3), O···HN 2.435 (2) Å]. The torsion angles C2—C1—C12—N1 and C2—C1—C13—N2 are 78.4 (3) and −131.9 (4)°, respectively, in (1), C2—C1—C12—O and C2—C1—C13—N are 89.2 (2) and −124.5 (3)°, respectively, in (2), and C2—C1—C8—O