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Structures of Two Novel Heptacyclic Compounds: a Cage Ketone and a Cage Enone

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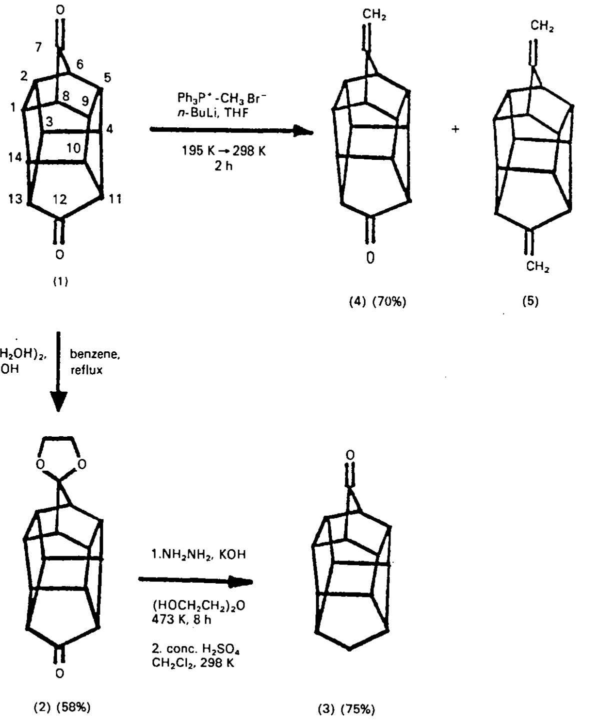
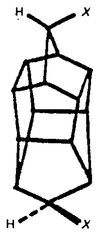
Abstract. Heptacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]tetradecan-7-one (3), $C_{14}H_{14}O$, $M_r = 198{\cdot}27$, orthorhombic, *Pcca*, $a = 8{\cdot}681\,(2)$, $b = 12{\cdot}694\,(2)$, $c = 8{\cdot}622\,(2)$ Å, $V = 950{\cdot}1\,(2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}386$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 0{\cdot}79$ cm^{-1}, $F(000) = 424$, $T = 295$ K, $R = 0{\cdot}0696$ for 680 reflections. 17-Methyleneheptacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]tetradecan-12-one (4), $C_{15}H_{14}O$, $M_r = 210{\cdot}28$, orthorhombic, *Cmc*2$_1$, $a = 6{\cdot}793\,(2)$, $b = 12{\cdot}245\,(3)$, $c = 12{\cdot}216\,(3)$ Å, $V = 1016{\cdot}2\,(4)$ Å^3, $Z = 4$, $D_x = 1{\cdot}374$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 0{\cdot}78$ cm^{-1}, $F(000) = 448$, $T = 298$ K, $R = 0{\cdot}0417$ for 567 reflections. The basic cage structures of compounds (3) and (4) can be described as arising from the cross dimerization of norbornadiene and are composed of eight fused five-membered rings all exhibiting chair conformations. Molecular mechanics calculations give $\Delta H_f = -36{\cdot}2$ and $72{\cdot}46$ kJ mol^{-1} and $E(\text{strain}) = 227{\cdot}6$ and $245{\cdot}5$ kJ mol^{-1} for (3) and (4), respectively. The molecules exhibit C_{2v} symmetry; however, space-group symmetry requires only a twofold axis in (3) and a mirror plane in (4).

Introduction. As part of a program that is concerned with the synthesis of novel, substituted heptacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}0^{5,9}.0^{10,14}]tetradecanes (HCTD) (Marchand & Hayes, 1977; Marchand & Earlywine, 1984; Marchand & Wu, 1985), transformations of HCTD-7,12-dione (1) (Marchand & Earlywine, 1984) have been studied. Thus, reaction of a benzene solution of (1) with ethylene glycol (1 equivalent) in the presence of a catalytic amount of *p*-toluenesulfonic acid in a Dean–Stark apparatus afforded the corresponding mono(ethylene ketal), (2) (see scheme). Wolff–Kishner reduction of the ketone carbonyl group in (2) followed by acid hydrolysis afforded HCTD-7-one (3). Wittig reaction of (1) with one equivalent of triphenylphosphonium methylide afforded two products. The major product of this reaction, as expected, was the corresponding enone (4), which was formed in 70% yield along with a small amount of the corresponding diene, (5) (see scheme). The structures of (3) and (4) have been elucidated *via* single-crystal X-ray crystallography.





(6) (X = H)
(7) (X = O*t* − Bu)

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Experimental. All data were collected on a Nicolet $R3m/\mu$ update of a $P2_1$ diffractometer using the ω-scan mode, a variable scan rate (4 to 29·5° $\min^{-1}$) and graphite-monochromated Mo $K\alpha$ radiation. Lattice parameters were obtained from a least-squares refinement of 25 reflections. Monitored reflections showed maximum random variations in intensities of ± 2% for (3) and (4), respectively and data were scaled accordingly. Lorentz–polarization corrections and ψ-scan-based empirical absorption corrections were applied. The structures were solved by direct methods and refined by a block-cascade least-squares technique. H atoms were located in difference maps and were refined with isotropic thermal parameters. $\sum w(|F_o| - |F_c|)^2$ was minimized with $w = [\sigma^2(F_o) + gF_o^2]^{-1}$. All computer programs were supplied by Nicolet for Desktop 30 Microeclipse and Nova 4/C configuration (Nicolet Instrument Corporation, 1986) while atomic scattering factors and anomalous-dispersion corrections were from *International Tables for X-ray Crystallography* (1974). Table 1 lists the crystal data, experimental parameters and refinement data.

Very poor quality crystals of compound (3) were available and the structure was solved initially utilizing a large crystal which gave very broad diffuse asymmetric peaks. The structure refined poorly and difference maps indicated a disordered structure with the C(1) and C(8) ends of the molecule partially exchanged. Several additional crystals provided structures with varying degrees of disorder. One crystal gave good peak profiles and the data refined to $R = 0{\cdot}069$. A difference map showed a peak of 0·64 e $Å^{-3}$ lying on the twofold axis between the two C(1) H atoms and 1·05 Å from the carbon. Refinement of this position lowered the R factor slightly but the occupancy factor was not statistically significant. While this is consistent with a small degree of disorder, it has no statistically significant effect upon the structure. Table 2 contains a listing of atomic positional parameters while Table 3 gives interatomic distances and valence angles for (3).

Crystals of compound (4) were also of poor quality and peak scans showed asymmetric peaks. Table 4 lists atomic positional parameters while Table 5 gives bond distances and valence angles. Figs. 1 and 2 are drawings of compounds (3) and (4).*

Discussion. The basic cage structure of molecules (3) and (4) is formed by the cross dimerization of two norbornadiene molecules and contains eight five-

Table 1. *Crystal data, experimental parameters and refinement data*

	(3)	(4)
Crystal dimensions (mm)	0·52 × 0·35 × 0·15	0·38 × 0·25 × 0·18
Color	Colorless	Colorless
Lattice parameters 2θ range (°)	23·36 29·12	22·45–30·87
Systematic extinctions	$0kl$ $l = 2n + 1$ $h0l$ $l = 2n + 1$ $hk0$ $h = 2n + 1$	hkl $h + k = 2n + 1$ $h0l$ $l = 2n + 1$
Space group	$Pcca$	$Cmc2_1$
Data collection range	$3 \le 2\theta \le 55$	$3 \le 2\theta \le 55$
hkl range	0,11; 0,16; 0,11	0,8; 0,15; 0,15
Monitored reflections	$\bar{3}3\bar{3}$, $11\bar{3}$	$3\bar{1}1$, $11\bar{4}$
Total reflections	1288	1383
Independent reflections	1092	662
$R_{\rm int}$	0·008	0·011
Reflections $\ge 3\sigma(I)$	680	567
Transmission factors	0·946 0·895	0·958–0·921
R (R all data)	0·069 (0·097)	0·0417 (0·0503)
wR (wR all data)	0·078 (0·101)	0·0503 (0·0519)
Number of parameters	99	112
S	1·483	1·278
$(\Delta/\sigma)_{\rm max}$	0·004	0·002
Largest peaks in final difference map (e $Å^{-3}$)	0·64, −0·36	0·20, −0·22
g(weights)	0·00262	0·0083
x(isotropic extinction)*	0·011 (4)	0·0011 (5)

* $F = F_c/[1{\cdot}0 + 0{\cdot}002xF_c^2/\sin(2\theta)]^{0{\cdot}25}$ (Nicolet Instrument Corporation, 1986).

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

$U_{\rm eq}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U_{\rm eq}$
C(1)	5000	382 (3)	2500	46 (1)
C(2)	5934 (3)	1184 (2)	3410 (3)	38 (1)
C(3)	6587 (3)	1910 (2)	2150 (3)	33 (1)
C(4)	6602 (3)	3037 (2)	2788 (3)	33 (1)
C(5)	5921 (3)	3754 (2)	1545 (3)	36 (1)
C(6)	4659 (3)	3037 (2)	894 (3)	31 (1)
C(7)	5292 (3)	1909 (2)	891 (3)	34 (1)
C(8)	5000	4534 (3)	2500	38 (1)
O(8)	5000	5471 (2)	2500	63 (1)

Table 3. *Bond lengths* (Å) *and angles* (°) *for compound* (3)

C(1)—C(2)	1·519 (4)	C(1)—C(2A)	1·519 (4)
C(2)—C(3)	1·533 (4)	C(2)—C(7A)	1·529 (4)
C(3)—C(4)	1·531 (3)	C(3)—C(7)	1·562 (4)
C(4)—C(5)	1·524 (4)	C(4)—C(6A)	1·577 (3)
C(5)—C(6)	1·529 (3)	C(5)—C(8)	1·515 (3)
C(6)—C(7)	1·533 (3)	C(8)—O(8)	1·188 (5)
C(2)—C(1)—C(2A)	95·9 (3)	C(1)—C(2)—C(3)	103·5 (2)
C(1)—C(2)—C(7A)	103·6 (2)	C(3)—C(2)—C(7A)	100·1 (2)
C(2)—C(3)—C(4)	108·0 (2)	C(2)—C(3)—C(7)	103·1 (2)
C(4)—C(3)—C(7)	104·8 (2)	C(3)—C(4)—C(5)	107·5 (2)
C(3)—C(4)—C(6A)	104·7 (2)	C(5)—C(4)—C(6A)	103·7 (2)
C(4)—C(5)—C(6)	100·4 (2)	C(4)—C(5)—C(8)	102·3 (2)
C(6)—C(5)—C(8)	102·2 (2)	C(5)—C(6)—C(7)	107·4 (2)
C(5)—C(6)—C(4A)	103·4 (2)	C(7)—C(6)—C(4A)	104·4 (2)
C(3)—C(7)—C(6)	104·8 (2)	C(3)—C(7)—C(2A)	103·2 (2)
C(6)—C(7)—C(2A)	108·1 (2)	C(5)—C(8)—O(8)	130·8 (1)
C(5)—C(8)—C(5A)	98·4 (3)	O(8)—C(8)—C(5A)	130·8 (1)

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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 52679 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Atomic coordinates* (× 10⁴) *and isotropic thermal parameters* (Å² × 10³) *for compound* (4)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C(1)	1141 (4)	2879 (2)	3378 (4)	41 (1)
C(2)	1738 (4)	3533 (2)	2358 (4)	43 (1)
C(3)	0	4290 (3)	2076 (5)	47 (1)
C(4)	0	4264 (4)	859 (5)	56 (2)
O(4)	0	5004 (4)	192	80 (1)
C(5)	0	3039 (4)	682 (5)	46 (1)
C(6)	1732 (4)	2678 (3)	1399 (4)	43 (1)
C(7)	1144 (4)	1599 (2)	1936 (4)	40 (1)
C(8)	1673 (4)	1671 (3)	3161 (4)	41 (1)
C(9)	0	1065 (3)	3695 (5)	42 (1)
C(10)	0	245 (4)	4395 (5)	60 (2)

Table 5. *Bond lengths* (Å) *and angles* (°) *for compound* (4)

C(1)—C(2)	1·537 (6)	C(1)—C(8)	1·545 (4)
C(1)—C(1*A*)	1·552 (6)	C(2)—C(3)	1·541 (4)
C(2)—C(6)	1·573 (6)	C(3)—C(4)	1·489 (9)
C(3)—C(2*A*)	1·541 (4)	C(4)—O(4)	1·219 (7)
C(4)—C(5)	1·516 (7)	C(5)—C(6)	1·534 (5)
C(5)—C(6*A*)	1·534 (5)	C(6)—C(7)	1·528 (5)
C(7)—C(8)	1·544 (7)	C(7)—C(7*A*)	1·556 (6)
C(8)—C(9)	1·507 (5)	C(9)—C(10)	1·320 (7)
C(9)—C(8*A*)	1·507 (5)		
C(2)—C(1)—C(8)	107·3 (3)	C(2)—C(1)—C(1*A*)	105·3 (2)
C(8)—C(1)—C(1*A*)	103·5 (2)	C(1)—C(2)—C(3)	107·0 (3)
C(1)—C(2)—C(6)	104·9 (3)	C(3)—C(2)—C(6)	103·4 (4)
C(2)—C(3)—C(4)	102·2 (4)	C(2)—C(3)—C(2*A*)	100·2 (4)
C(4)—C(3)—C(2*A*)	102·2 (4)	C(3)—C(4)—O(4)	130·8 (5)
C(3)—C(4)—C(5)	99·4 (4)	O(4)—C(4)—C(5)	129·8 (6)
C(4)—C(5)—C(6)	101·8 (3)	C(4)—C(5)—C(6*A*)	101·8 (3)
C(6)—C(5)—C(6*A*)	100·3 (4)	C(2)—C(6)—C(5)	103·7 (3)
C(2)—C(6)—C(7)	104·8 (4)	C(5)—C(6)—C(7)	107·1 (3)
C(6)—C(7)—C(8)	107·8 (3)	C(6)—C(7)—C(7*A*)	105·2 (2)
C(8)—C(7)—C(7*A*)	103·5 (2)	C(1)—C(8)—C(7)	99·6 (3)
C(1)—C(8)—C(9)	102·7 (3)	C(7)—C(8)—C(9)	102·5 (3)
C(8)—C(9)—C(10)	131·0 (2)	C(8)—C(9)—C(8*A*)	98·0 (4)
C(10)—C(9)—C(8*A*)	131·0 (2)		

membered rings. The five-membered rings exhibit envelope conformations. The parent hydrocarbon should exhibit D_{2d} symmetry in the gas phase while compounds (3) and (4) should have C_{2v} symmetry. In the solid state distances and angles are consistent with C_{2v} symmetry for (3) and (4) although space-group symmetry requires only a twofold axis for (3) and a mirror plane for (4). The bond lengths in (3) and (4) are equivalent although (4) contains an exocyclic methylene. The bonds in these cages can be classified in terms of those within the original norbornane molecules and the new bonds joining these units, *e.g.* C(3)—C(4) in (3). In norbornane (Doms, Van Hemelrijk, Van de Mieroop, Lenstra & Geise, 1985; Doms, Van den Enden, Geise & Van Alsenoy, 1985) the ethane bridges [C(4)—C(6*A*) in (3)] are longer than the connecting bonds [C(4)—C(5) in (3)] which in turn are longer than the methylene bridge bonds [C(5)—C(8) in (3)]. In the cage structures the ethane bonds average 1·569 (8) and 1·560 (11) Å and the connecting bonds 1·529 (4) and 1·541 (4) Å for (3) and (4), respectively. The methylene bridge bonds containing the keto functionality are 1·515 (5) Å in (3) and average 1·502 (14) Å in (4), while the bonds

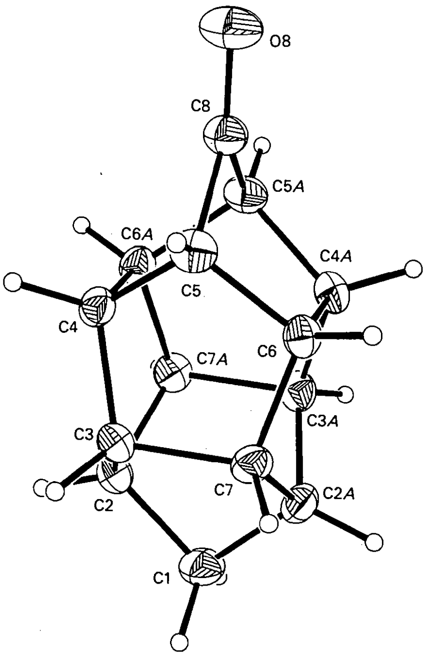

Fig. 1. Compound (3) with thermal ellipsoids drawn at the 30% probability level. H atoms are represented by spheres of arbitrary size.

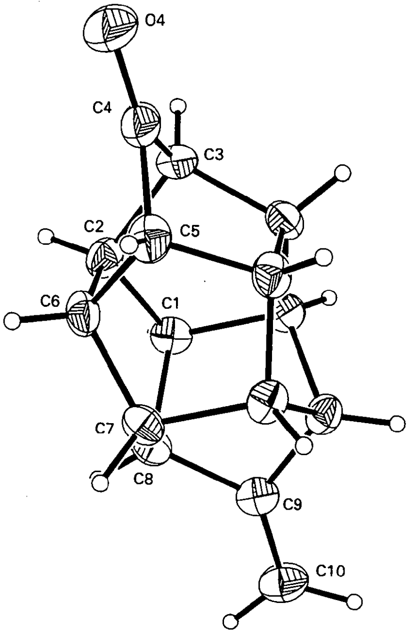

Fig. 2. Compound (4) with thermal ellipsoids drawn at the 30% probability level. H atoms are represented by spheres of arbitrary size.

around the exocyclic methylene are 1·507 (5) Å in (4). The methylene bridge bonds around the unsubstituted methylene in (3) are 1·519 (4) Å. The bonds joining the two norbornane moieties average 1·532 (2) and 1·532 (5) Å in (3) and (4), respectively. In general, for molecular mechanics programs such as *MM*2 the ethane bond lengths are significantly underestimated (Doms, Van Hemelrijk, Van de Mieroop, Lenstra & Geise, 1985; Doms, Van den Enden, Geise & Van Alsenoy, 1985) although comparative energy calculations remain valid; however, *PCMODEL* (1989) calculations for (3) and (4) using program-generated parameters show better bond-length agreement than in norbornane itself. In norbornane the addition of a torsion-stretch interaction has led to excellent agreement between observed and calculated distances and angles (Allinger, Geise, Pyckhout, Paquette & Gallucci, 1989). Molecular mechanics calculations give strain energies of 227·6 and 245·5 kJ mol^{-1} for (3) and (4), respectively, with the main difference due to angle strain associated with the exocyclic methylene moiety, *i.e.* C(8)—C(9)—C(8*A*) = 98·0 (4) at the C(sp^2) center. The structures of the parent hydrocarbon, (6) (Chow, Liu & Chao, 1985) and a di-*tert*-butoxy derivative, (7) (Neely, van der Helm, Marchand & Hayes, 1976) have been reported and average values for the chemically equivalent bonds are statistically equivalent to those reported here.

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Structure of Muscarine Chloride

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Abstract. Trimethyl(tetrahydro-4-hydroxy-5-methyl-2-furyl)methylammonium chloride, $C_9H_{20}NO_2^+.Cl^-$, $M_r = 209·7$, orthorhombic, $P2_12_12$, at $T = 105$ K: $a = 9·731$ (3), $b = 9·801$ (1), $c = 11·478$ (3) Å, $V = 1094·7$ (4) Å^3, $Z = 4$, $D_x(105\ \text{K}) = 1·272$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0·319$ mm^{-1}, $F(000) = 456$, m.p. (hot-stage microscope) = 446–449 K (corrected), $R = 0·033$ for 3013 observed [$I \geq 3·0\sigma(I)$] reflections. Crystals were grown from a solution of (±)-muscarine chloride, but the single crystal is chiral. The tetrahydrofuran ring conformation is intermediate between envelope ^3E and twist $^3T_4$ and is different from the one known from the crystal structure of muscarine iodide. For muscarine chloride τ(C—O—C—C) is 112·9 (1)° and τ(O—C—C—N) is 76·8 (2)°. The crystal packing is stabilized by hydrogen bonds O—H···Cl$^-$ and by weaker electrostatic and van der Waals contacts.

Introduction. Muscarine mimics the function of the neurotransmitter acetylcholine in the muscarinic part of the cholinergic nervous system. Muscarine contains a five-membered ring, which makes it less flexible than acetylcholine, but muscarine is still only semirigid. The crystal structure of (+)-muscarine iodide (MUSCAI) has been known since 1957

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