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Structures of Two Tricyclo[5.2.1.0^{2,6}]decane Derivatives

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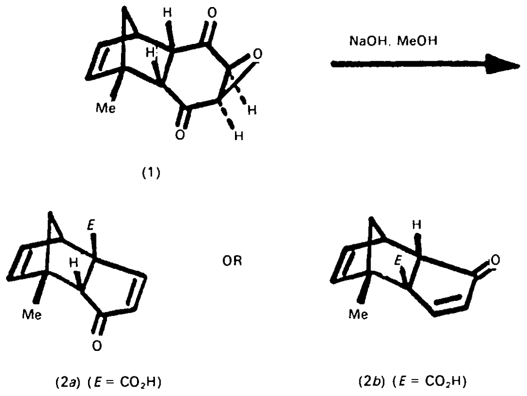
Abstract. 1-Methyl-3-oxotricyclo[5.2.1.0^{2,6}]dec-4,8-diene-6-carboxylic acid (2*a*), $C_{12}H_{12}O_3$, $M_r = 204{\cdot}22$, monoclinic, $P2_1/c$, $a = 11{\cdot}773\,(1)$, $b = 7{\cdot}069\,(1)$, $c = 12{\cdot}295\,(1)$ Å, $\beta = 91{\cdot}13\,(1)^\circ$, $V = 1023{\cdot}0\,(2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}330$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 1{\cdot}00$ cm^{-1}, $F(000) = 432$, $T = 295$ K, $R = 0{\cdot}0523$ for 1679 reflections with $I > 3\sigma(I)$. 5-Methyl-3-oxotricyclo[5.2.1.0^{2,6}]dec-8-ene-6-carboxylic acid (5*b*), $C_{12}H_{14}O_3$, $M_r = 206{\cdot}24$, orthorhombic, *Pbca*, $a = 7{\cdot}807\,(1)$, $b = 12{\cdot}872\,(2)$, $c = 20{\cdot}950\,(3)$ Å, $V = 2105{\cdot}3\,(5)$ Å^3, $Z = 8$, $D_x = 1{\cdot}301$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 0{\cdot}87$ cm^{-1}, $F(000) = 880$, $T = 298$ K, $R = 0{\cdot}0516$ for 1140 reflections with $I > 3\sigma(I)$. The two compounds contain a norbornene moiety fused to a five-membered ketone ring. The norbornenes exhibit a folding along the double bond of 7 (1) and 6 (1)° for (2*a*) and (5*b*), respectively. Compound (2*a*) forms hydrogen-bonded acid dimers in the solid while (5*b*) forms hydrogen bonds between the acid group of one molecule and the keto group of another. Molecular mechanics calculations predict the strain energies of (2*a*) and (5*b*) to be 136·4 and 145·0 kJ mol^{-1}.

Introduction. Functionalized tricyclo[5.2.1.0^{2,6}]-decanes have been utilized extensively as intermediates in the synthesis of substituted cyclopentenones and polycyclopentanoid natural products (Klunder, Bos, Verlaak & Zwanenburg, 1981; Klunder, Bos & Zwanenburg, 1981; Klunder, van Gastel & Zwanenburg, 1988; Lange, Klunder & Zwanenburg, 1988; Marchand & Vidyasagar, 1988; Smith, Marchand, Suri & Jin, 1986; Verlaak, Klunder & Zwanenburg, 1982). In addition, Cope rearrangements of derivatives of this ring system have been studied extensively (Klunder, Lange & Zwanenburg, 1987; Suri, Rodgers & Lauderdale, 1988). Current interest in the total synthesis of triquinane natural products (Smith, Marchand, Suri & Jin, 1986) has led to the synthesis and structural characterization of two substituted tricyclo[5.2.1.0^{2,6}]decanes.

The first of these compounds was synthesized *via* Favorskii-type ring contraction of the tetracyclic epoxide (1) (Herz, Iyer & Nair, 1975). This reaction potentially could afford two ring-contracted products, *i.e.* (2*a*) and/or (2*b*) (see Scheme 1); however, the reaction proceeded regiospecifically to afford a single product whose structure is shown by X-ray analysis to be (2*a*).



Scheme 1

Once the structure of (2*a*) had been established, it was of interest to carry out β-alkylation of the enone moiety by using Me_2CuLi (House, Chu, Wilkins & Umen, 1975). Thus, reaction of (2*a*) with $CuBr.SMe_2$—MeLi produced two products, (3*a*) and (3*b*), whose structures were assigned by one- and two-dimensional NMR spectroscopic methods (Scheme 1; Smith, Marchand, Suri & Jin, 1986). Recently, the corresponding reaction of a desmethyl derivative of (2*a*) [*i.e.* (4)] was studied. Two products, (5*a*) and (5*b*), were obtained from this reaction (see

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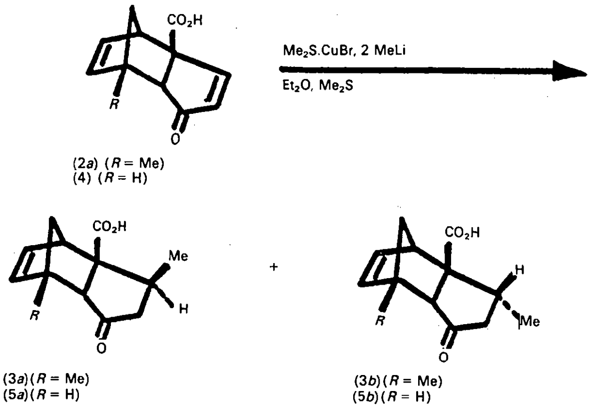
Scheme 2). X-ray analysis of the minor product of the reaction showed it to have the structure (*5b*).



(2*a*) (*R* = Me)
(4) (*R* = H)

(3*a*)(*R* = Me)
(5*a*)(*R* = H)

(3*b*)(*R* = Me)
(5*b*)(*R* = H)

Scheme 2

Experimental. All data were collected on a Nicolet *R*3*M*/*μ* update of a $P2_1$ diffractometer using the *ω*-scan technique with a variable scan rate of 4 to 29·3° min^{-1}. Lattice parameters were obtained from a least-squares refinement of 25 reflections. Lorentz and polarization corrections were applied and a *ψ*-scan-based empirical absorption correction was made on both sets. The structures were solved by direct methods and refined by a block-cascade least-squares refinement. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = [\sigma^2(F_o) + gF_o^2]^{-1}$. An isotropic extinction correction, $F = F_c/[1{\cdot}0 + 0{\cdot}002x.0022\,(3)F_c^2/\sin(2\theta)]^{0{\cdot}25}$ (Nicolet Instrument Corporation, 1986) was applied to compound (2*a*).

In compound (2*a*) all H atoms were located in a difference map and were refined with isotropic thermal parameters except for the methyl H atoms which were allowed to ride on the attached carbon. In compound (5*b*) all H atoms were located in a difference map and were allowed to ride on the attached atom except for the H atoms of the C—C double bond and the H atoms involved in hydrogen bonding. Crystal, data collection and refinement parameters are included in Table 1. 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). Tables 2 and 4 contain atomic positional parameters for compounds (2*a*) and (5*b*) while Tables 3 and 5 list interatomic distances and valence angles for the two compounds.*

Table 1. *Crystal, data collection and refinement data*

	(2*a*)	(5*b*)
Crystal size (mm)	0·45 × 0·25 × 0·20	0·25 × 0·50 × 0·50
Color	Colorless	Colorless
Lattice parameters 2*θ* range (°)	22·93–29·03	22·15–29·70
Systematic absences	*h*0*l* *l* = 2*n* + 1 0*k*0 *k* = 2*n* + 1	0*kl* *k* = 2*n* + 1 *h*0*l* *l* = 2*n* + 1 *hk*0 *h* = 2*n* + 1
Data collection 2*θ* range (°)	3–55	3–45
hkl range	− 15,15;0,9;0,15	0,8;0,13;0,22
Monitored reflections	$31\bar{2}$, $2\bar{1}\bar{3}$	$0\bar{6}\bar{2}$, $20\bar{8}$
Total reflections	2660	1633
Independent reflections	2344	1379
R_{int}	0·0130	0·008
Reflections ≥ 3*σ*(*I*)	1679	1140
Transmission factors	0·958–0·925	0·914–0·950
R (*R* all data)	0·0523 (0·0784)	0·0516 (0·0621)
wR (*wR* all data)	0·0470 (0·0499)	0·0636 (0·0649)
Number parameters	176	159
S	1·553	2·010
$(\Delta/\sigma)_{\max}$	0·010	0·004
Largest peaks in difference map (e Å^{-3})	0·24, −0·17	0·33, −0·22
g (weights)	0·00018	0·00044

Table 2. *Atomic coordinates* (× 10^4) *and isotropic thermal parameters* (Å^2 × 10^3) *for compound* (2*a*)

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

	x	*y*	*z*	U_{eq}
C(1)	2471 (2)	5900 (3)	1340 (2)	38 (1)
C(2)	2474 (2)	3714 (3)	1569 (1)	32 (1)
C(3)	3593 (2)	2937 (3)	2001 (2)	39 (1)
O(3)	4052 (1)	3370 (2)	2858 (1)	61 (1)
C(4)	4022 (2)	1613 (3)	1195 (2)	45 (1)
C(5)	3337 (2)	1552 (3)	331 (2)	39 (1)
C(6)	2322 (1)	2822 (3)	436 (1)	31 (1)
C(7)	2280 (2)	4615 (3)	− 332 (2)	38 (1)
C(8)	3432 (2)	5527 (3)	− 253 (2)	42 (1)
C(9)	3543 (2)	6283 (3)	717 (2)	42 (1)
C(10)	1609 (2)	5940 (3)	387 (2)	43 (1)
C(11)	2244 (2)	7113 (3)	2323 (2)	61 (1)
C(12)	1265 (2)	1650 (3)	268 (2)	34 (1)
O(1)	655 (1)	1185 (2)	1020 (1)	54 (1)
O(2)	1070 (1)	1126 (2)	− 719 (1)	58 (1)

Discussion. Figs. 1 and 2 are drawings of compounds (2*a*) and (5*b*). Both molecules contain a norbornene moiety fused to a five-membered ring. A carboxylate group is fused at the ring juncture *syn* to the methylene bridge of the norbornene. The molecules differ in the position of a methyl group and in the saturation of the five-membered ketone ring. The norbornene system of (5*b*) is symmetric about a pseudo mirror plane passing through the molecule while (2*a*) shows considerable asymmetry, *e.g.* C(1)—C(10) = 1·535 (3) and C(7)—C(10) = 1·519 (3) Å. The C(1)—C(2) and C(6)—C(7) bonds in (2*a*) of 1·571 (3) and 1·581 (3) Å are longer than the values of 1·559 (4) and 1·555 (4) Å found in (5*b*). These variations in distances are not reflected in molecular mechanics calculations (Allinger & Yu, 1980), and, if real, may be related to intermolecular

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52683 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bond lengths* (Å) *and valence angles* (°) *for compound* (2*a*)

C(1)—C(2)	1·571 (3)	C(1)—C(9)	1·513 (3)
C(1)—C(10)	1·535 (3)	C(1)—C(11)	1·510 (3)
C(2)—C(3)	1·513 (3)	C(2)—C(6)	1·537 (2)
C(3)—O(3)	1·214 (2)	C(3)—C(4)	1·460 (3)
C(4)—C(5)	1·321 (3)	C(5)—C(6)	1·503 (3)
C(6)—C(7)	1·581 (3)	C(6)—C(12)	1·505 (2)
C(7)—C(8)	1·504 (3)	C(7)—C(10)	1·519 (3)
C(8)—C(9)	1·311 (3)	C(12)—O(1)	1·226 (2)
C(12)—O(2)	1·285 (2)		

C(2)—C(1)—C(9)	105·5 (1)	C(2)—C(1)—C(10)	98·9 (1)
C(9)—C(1)—C(10)	99·0 (1)	C(2)—C(1)—C(11)	114·5 (2)
C(9)—C(1)—C(11)	117·8 (2)	C(10)—C(1)—C(11)	118·4 (2)
C(1)—C(2)—C(3)	114·8 (2)	C(1)—C(2)—C(6)	104·0 (1)
C(3)—C(2)—C(6)	104·7 (1)	C(2)—C(3)—O(3)	125·6 (2)
C(2)—C(3)—C(4)	107·8 (2)	O(3)—C(3)—C(4)	126·6 (2)
C(3)—C(4)—C(5)	110·7 (2)	C(4)—C(5)—C(6)	112·7 (2)
C(2)—C(6)—C(5)	104·1 (1)	C(2)—C(6)—C(7)	102·4 (1)
C(5)—C(6)—C(7)	116·3 (1)	C(2)—C(6)—C(12)	115·6 (1)
C(5)—C(6)—C(12)	108·4 (1)	C(7)—C(6)—C(12)	110·1 (1)
C(6)—C(7)—C(8)	106·7 (1)	C(6)—C(7)—C(10)	99·0 (1)
C(8)—C(7)—C(10)	100·2 (2)	C(7)—C(8)—C(9)	107·9 (2)
C(1)—C(9)—C(8)	108·6 (2)	C(1)—C(10)—C(7)	95·2 (2)
C(6)—C(12)—O(1)	122·6 (2)	C(6)—C(12)—O(2)	114·9 (2)
O(1)—C(12)—O(2)	122·5 (2)		

Table 5. *Bond distances* (Å) *and valence angles* (°) *for compound* (5*b*)

C(1)—C(2)	1·559 (4)	C(1)—C(9)	1·512 (4)
C(1)—C(10)	1·539 (4)	C(2)—C(3)	1·489 (4)
C(2)—C(6)	1·539 (4)	C(3)—O(3)	1·215 (3)
C(3)—C(4)	1·503 (4)	C(4)—C(5)	1·519 (4)
C(5)—C(6)	1·570 (4)	C(5)—C(11)	1·503 (4)
C(6)—C(7)	1·555 (4)	C(6)—C(12)	1·513 (4)
C(7)—C(8)	1·514 (4)	C(7)—C(10)	1·540 (4)
C(8)—C(9)	1·324 (5)	C(12)—O(1)	1·194 (4)
C(12)—O(2)	1·323 (3)		

C(2)—C(1)—C(9)	107·7 (2)	C(2)—C(1)—C(10)	99·8 (2)
C(9)—C(1)—C(10)	99·0 (2)	C(1)—C(2)—C(3)	113·2 (2)
C(1)—C(2)—C(6)	103·6 (2)	C(3)—C(2)—C(6)	106·9 (2)
C(2)—C(3)—O(3)	124·6 (3)	C(2)—C(3)—C(4)	110·0 (2)
O(3)—C(3)—C(4)	125·5 (3)	C(3)—C(4)—C(5)	105·6 (2)
C(4)—C(5)—C(6)	105·4 (2)	C(4)—C(5)—C(11)	115·1 (3)
C(6)—C(5)—C(11)	115·4 (2)	C(2)—C(6)—C(5)	105·7 (2)
C(2)—C(6)—C(7)	102·4 (2)	C(5)—C(6)—C(7)	118·3 (2)
C(2)—C(6)—C(12)	114·8 (2)	C(5)—C(6)—C(12)	107·1 (2)
C(7)—C(6)—C(12)	108·9 (2)	C(6)—C(7)—C(8)	109·7 (2)
C(6)—C(7)—C(10)	99·2 (2)	C(8)—C(7)—C(10)	99·6 (2)
C(7)—C(8)—C(9)	107·2 (3)	C(1)—C(9)—C(8)	108·0 (3)
C(1)—C(10)—C(7)	93·3 (2)	C(6)—C(12)—O(1)	124·3 (3)
C(6)—C(12)—O(2)	112·9 (2)	O(1)—C(12)—O(2)	122·7 (3)

Table 4. *Atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters* ($Å^2 \times 10^3$) *for compound* (5*b*)

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

	x	y	z	U_{eq}
C(1)	−3449 (4)	6073 (2)	3613 (1)	53 (1)
C(2)	−1782 (4)	6116 (2)	3204 (1)	44 (1)
C(3)	−1158 (4)	7193 (2)	3090 (1)	47 (1)
O(3)	−1821 (3)	7807 (2)	2725 (1)	66 (1)
C(4)	387 (4)	7405 (2)	3497 (2)	55 (1)
C(5)	1114 (4)	6347 (2)	3668 (1)	47 (1)
C(6)	−441 (3)	5575 (2)	3628 (1)	35 (1)
C(7)	−1473 (4)	5349 (2)	4247 (1)	48 (1)
C(8)	−2016 (4)	6362 (2)	4554 (2)	52 (1)
C(9)	−3200 (4)	6780 (2)	4181 (2)	55 (1)
C(10)	−3189 (4)	5019 (2)	3946 (2)	54 (1)
C(11)	2121 (4)	6308 (3)	4278 (2)	62 (1)
C(12)	241 (4)	4561 (2)	3366 (1)	43 (1)
O(1)	646 (3)	3836 (2)	3687 (1)	71 (1)
O(2)	398 (3)	4566 (1)	2737 (1)	64 (1)

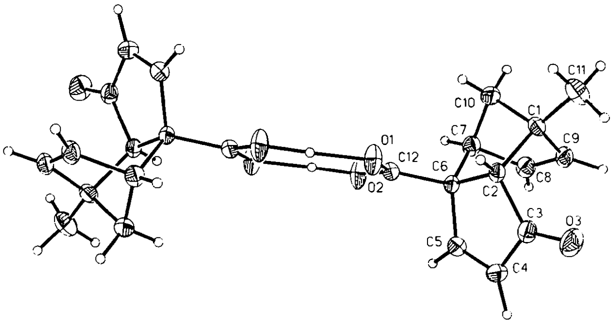

Fig. 1. Compound (2*a*) with thermal ellipsoids drawn at the 25% probability level. H atoms are represented by spheres of arbitrary size.

interactions. As can be seen in Fig.1, molecule (2*a*) forms a typical hydrogen-bonded acid dimer. The two C(12)—O distances are not equivalent, 1·226 (2) and 1·285 (2) Å; with O(2)—H(20) = 1·16 (3) Å, H(20)···O(1′) $(-x, -y, -z)$ = 1·47 (3) Å, O(2)···O(1′) = 2·627 (2) Å and O(2)—H(20)···O(1′) = 176 (1)°. Compound (5*b*) also forms a hydrogen bond; however, the bond now involves the acid hydrogen and the keto group at C(3), H(2)···O(3) $(-x, -\frac{1}{2}+y, \frac{1}{2}-z)$ = 1·98 (4) Å, O(2)···O(3) = 2·701 (3) Å, O(2)—H(2)···O(3) = 168 (1)°. The C(12)—O(1) and C(12)—O(2) distances of 1·194 (4) and 1·323 (3) Å correspond more closely to a normal monomeric acid moiety.

The norbornene double bond shows the normal folding (Watson, 1983; Watson, Galloy, Bartlett &

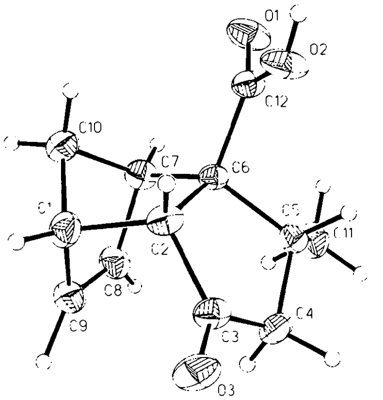

Fig. 2. Compound (5*b*) with thermal ellipsoids drawn at the 30% probability level. H atoms are represented by spheres of arbitrary size.

Roof, 1981) with the angle between least-squares planes C(1)C(9)C(8)C(7) (0·002 and 0·005 Å r.m.s. deviation) and H(8)C(8)C(9)H(9) (0·008 and 0·001 Å r.m.s. deviation) of 7 (1) and 6 (1)° for (2*a*) and (5*b*), respectively. The C(4)—C(5) double bond does not have the prerequisites for folding and the corresponding folding angle of 2 (1)° is not statistically different from 0·0°.

Molecular mechanics calculations (Allinger & Yuh, 1980) give heats of formation of $-333{\cdot}1$ and $-457{\cdot}5$ kJ mol^{-1} for (2*a*) and (5*b*), respectively. The strain energy for (2*a*) is 136·4 kJ mol^{-1} which is 11 kJ mol^{-1} less strained than (2*b*); however, (5*b*) has a strain energy of 145·0 kJ mol^{-1} which is about 7 kJ mol^{-1} less strained than the major isomer (5*a*).

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Absolute Configuration of (−)-4-Bromo-*N*-(*cis*-2-phenylcycloheptyl)benzamide

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Abstract. $C_{20}H_{22}BrNO$, $M_r = 372{\cdot}13$, orthorhombic, $P2_12_12_1$, $a = 5{\cdot}599$ (1), $b = 16{\cdot}888$ (3), $c = 18{\cdot}531$ (3) Å, $Z = 4$, $V = 1752$ (1) Å^3, $D_x = 1{\cdot}411$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 3{\cdot}227$ mm^{-1}, $F(000) = 776$, $T = 293$ K, final $R = 0{\cdot}030$ for 1961 observed reflections. Under enantiomeric and diastereomeric control 2-substituted cycloheptanones were converted by reductive amination and hydrogenolysis to *cis*-2-substituted cycloheptanamine hydrochlorides. The absolute configuration of one of these products, (+)-*cis*-2-phenylcycloheptanamine hydrochloride, is elucidated as (1*S*,2*S*) by X-ray structure analysis of its 4-bromo-*N*-benzamide, which corroborates the results

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