Table 3. *Intermolecular hydrogen bonds*

N(1)···O(8i)	2·900 (3) Å	N(4)···O(9ii)	2·895 (3) Å
N(1)—H(11)	0·84 (3) Å	N(4)—H(41)	0·87 (3) Å
H(11)···O(8i)	2·16 (3) Å	H(41)···O(9ii)	2·08 (3) Å
N(1)—H(11)···O(8i)	147 (2)°	N(4)—H(41)···O(9ii)	174 (2)°

Symmetry code: (i) x, $\frac{1}{2}-y$, $z-\frac{1}{2}$; (ii) $-x$, $-y$, $1-z$.

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Functionalized Bicyclo[4.4.0]decane from Double Michael Addition Reaction

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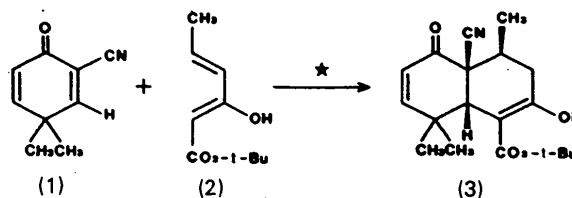
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Abstract. rel-(1R,5S,6R)-tert-Butyl 6-cyano-3-hydroxy-5,10,10-trimethyl-7-oxobicyclo[4.4.0]deca-2,8-diene-2-carboxylate. $C_{19}H_{25}NO_4$, $M_r = 331·41$, triclinic, $P\bar{1}$, $a = 8·0554$ (15), $b = 11·9774$ (24), $c = 20·361$ (4) Å, $\alpha = 87·585$ (18), $\beta = 86·941$ (16), $\gamma = 75·015$ (18)°, $Z = 4$, $V = 1894·12$ Å^3, $D_x = 1·162$ Mg m^{-3}, $\lambda(Cu\,K\alpha) = 1·54056$ Å, $\mu = 0·62$ mm^{-1}, $F(000) = 711·90$, room temperature, final $R = 0·065$, $wR = 0·037$, $S = 2·467$ for 4473 observed reflections. The bicyclic compound (3) is obtained from the double Michael addition reaction between a diene and a dienophile with total control of relative stereochemistry at carbons 1, 5 and 6. The relative stereochemistry is cis for the AB ring junction and syn between C6-cyano and C5-methyl.

Introduction. The synthesis of complex organic molecules of biological interest such as steroids is partic-

ularly attractive when synthetic strategies give the possibility of reaching a high level of chemo-, regio-, diastereo- and enantioselectivity. The Michael addition reaction is a very useful reaction in organic synthesis, and a few studies (Stork, Winkler & Saccomano, 1983; Toma, 1981) have been made to point out which are the important factors involved when this reaction is used in cyclization. A study of the intramolecular Michael addition reaction was reported recently (Lavallée &

* Cs₂CO₃ in CH₃CN, 16 h at room temperature, 95% yield

Fig. 1. Synthesis scheme.

Table 1. *Final coordinates and B_{eq} values with e.s.d.'s in parentheses*

$$B_{eq} = (8/3)\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	B_{eq} (Å²)
Molecule 1				
O(1)	0·0311(3)	0·9084(3)	0·7464(2)	5·88
O(2)	0·5603(3)	0·6327(2)	0·4868(1)	4·76
O(3)	0·3182(3)	0·7766(2)	0·4835(1)	4·63
O(4)	0·6322(3)	0·5284(2)	0·5968(1)	4·56
N(1)	0·4293(4)	0·8897(3)	0·6736(2)	5·61
C(1)	0·2119(4)	0·7596(3)	0·6786(2)	3·11
C(2)	0·0397(5)	0·8300(3)	0·7091(2)	3·85
C(3)	0·1144(5)	0·7951(4)	0·6910(2)	4·13
C(4)	-0·1089(5)	0·7221(4)	0·6442(2)	4·43
C(5)	0·0421(5)	0·6660(3)	0·5998(2)	3·66
C(6)	0·1910(4)	0·7277(3)	0·6073(2)	2·95
C(7)	0·3649(4)	0·6615(3)	0·5792(2)	2·96
C(8)	0·4753(5)	0·5892(3)	0·6185(2)	3·40
C(9)	0·4469(5)	0·5712(4)	0·6905(2)	4·07
C(10)	0·2895(5)	0·6513(4)	0·7238(2)	3·67
C(11)	0·3256(7)	0·6822(5)	0·7925(3)	5·28
C(12)	0·3358(5)	0·8336(3)	0·6758(2)	3·75
C(13)	-0·0132(6)	0·6853(5)	0·5286(2)	5·32
C(14)	0·0900(6)	0·5348(4)	0·6145(2)	4·77
C(15)	0·4223(5)	0·6866(3)	0·5133(2)	3·77
C(16)	0·3662(7)	0·8330(4)	0·4223(3)	5·72
C(17)	0·2180(10)	0·9361(5)	0·4140(3)	10·38
C(18)	0·3970(7)	0·7538(5)	0·3658(3)	6·94
C(19)	0·5299(9)	0·8713(5)	0·4341(3)	8·92
Molecule 2				
O'(1)	0·8596(3)	0·4421(3)	0·7579(2)	6·38
O'(2)	1·3824(3)	0·1275(2)	1·0001(1)	4·74
O'(3)	1·1496(3)	0·2787(2)	1·0103(1)	3·79
O'(4)	1·4380(3)	0·0260(2)	0·8887(1)	4·79
N'(1)	1·2716(4)	0·3913(3)	0·8025(2)	5·46
C'(1)	1·0323(4)	0·2789(3)	0·8182(2)	3·09
C'(2)	0·8626(5)	0·3590(4)	0·7943(2)	4·17
C'(3)	0·7062(5)	0·3247(4)	0·8189(3)	5·02
C'(4)	0·7068(5)	0·2514(4)	0·8690(2)	5·06
C'(5)	0·8550(5)	0·1937(3)	0·9103(2)	3·74
C'(6)	1·0129(4)	0·2476(3)	0·8921(2)	2·93
C'(7)	1·1853(4)	0·1734(3)	0·9150(2)	2·72
C'(8)	1·2841(4)	0·0984(3)	0·8722(2)	3·46
C'(9)	1·2537(5)	0·0874(4)	0·8020(2)	4·08
C'(10)	1·0891(5)	0·1700(3)	0·7755(2)	3·73
C'(11)	1·1153(6)	0·1958(5)	0·7027(3)	5·47
C'(12)	1·1657(5)	0·3437(3)	0·8096(2)	3·71
C'(13)	0·8000(6)	0·2187(4)	0·9825(3)	5·23
C'(14)	0·8929(6)	0·0629(4)	0·9025(3)	4·88
C'(15)	1·2465(5)	0·1882(3)	0·9780(2)	3·31
C'(16)	1·1908(5)	0·3178(4)	1·0732(2)	4·15
C'(17)	1·0384(6)	0·4150(5)	1·0901(3)	5·79
C'(18)	1·2187(7)	0·2239(5)	1·1257(3)	7·20
C'(19)	1·3472(7)	0·3648(5)	1·0615(3)	8·49

Table 2. *Intermolecular bond lengths (Å), angles (°) and torsion angles (°) with e.s.d's in parentheses*

	Molecule 1	Molecule 2
O(1)-C(2)	1·219(5)	1·211(5)
O(2)-C(15)	1·240(5)	1·242(5)
O(3)-C(15)	1·329(5)	1·336(5)
O(3)-C(16)	1·472(6)	1·465(5)
O(4)-C(8)	1·347(4)	1·365(4)
N(1)-C(12)	1·129(5)	1·142(5)
C(1)-C(2)	1·539(5)	1·543(5)
C(1)-C(6)	1·545(6)	1·545(6)
C(1)-C(10)	1·570(6)	1·552(6)
C(1)-C(12)	1·494(5)	1·479(5)
C(2)-C(3)	1·477(6)	1·480(6)
C(3)-C(4)	1·312(6)	1·316(7)
C(4)-C(5)	1·503(6)	1·497(6)
C(5)-C(6)	1·579(5)	1·589(5)
C(5) C(13)	1·530(7)	1·533(7)
C(5) C(14)	1·539(6)	1·530(6)
C(6)-C(7)	1·516(5)	1·527(5)
C(7)-C(8)	1·342(5)	1·350(5)
C(7)-C(15)	1·440(6)	1·432(6)
C(8)-C(9)	1·488(6)	1·479(6)
C(9)-C(10)	1·524(6)	1·543(6)
C(10)-C(11)	1·522(7)	1·516(7)
C(16)-C(17)	1·490(8)	1·494(6)
C(16)-C(18)	1·492(8)	1·501(7)
C(16)- C(19)	1·537(9)	1·512(7)
C(15)-O(3)-C(16)	123·9(3)	124·9(3)
C(2)-C(1)-C(6)	110·9(3)	110·2(3)
C(2)-C(1)-C(10)	110·2(3)	110·4(3)
C(2)-C(1)-C(12)	108·1(3)	107·5(3)
C(6)-C(1)-C(10)	112·9(3)	112·2(3)
C(6)-C(1)-C(12)	107·5(3)	108·3(3)
C(10)-C(1)-C(12)	107·0(3)	108·1(3)
O(1)-C(2)-C(1)	122·3(4)	122·2(4)
O(1)-C(2)-C(3)	122·1(4)	123·5(4)
C(1)-C(2)-C(3)	115·6(3)	114·3(4)
C(2)-C(3)-C(4)	122·1(4)	122·5(4)
C(3)-C(4)-C(5)	128·1(4)	127·6(4)
C(4)-C(5)-C(6)	108·9(3)	109·7(3)
C(4)-C(5)-C(13)	108·4(3)	108·2(3)
C(4)-C(5)-C(14)	108·8(3)	108·6(4)
C(6)-C(5)-C(13)	107·8(3)	107·8(3)
C(6)-C(5)-C(14)	115·5(3)	115·0(3)
C(13)-C(5)-C(14)	107·4(4)	107·5(4)
C(1)-C(6)-C(5)	114·1(3)	113·9(3)
C(1)-C(6)-C(7)	108·6(3)	108·9(3)
C(5)-C(6)-C(7)	114·2(3)	114·1(3)
C(6)-C(7)-C(8)	119·6(4)	117·8(3)
C(6)-C(7)-C(15)	120·7(3)	121·4(4)
C(8)-C(7)-C(15)	119·1(3)	120·6(3)
O(4)-C(8)-C(7)	122·7(4)	122·2(4)
O(4)-C(8)-C(9)	111·8(3)	110·4(3)
C(7)-C(8)-C(9)	125·4(3)	127·2(3)
C(8)-C(9)-C(10)	117·2(3)	116·0(3)
C(1)-C(10)-C(9)	111·3(3)	110·1(3)
C(1)-C(10)-C(11)	113·4(4)	114·4(4)
C(9)-C(10)-C(11)	112·0(4)	110·1(3)
N(1)-C(12)- C(1)	179·9(5)	178·3(4)
O(2)-C(15)-O(3)	121·8(4)	121·7(4)
O(2)-C(15)-C(7)	123·7(4)	124·1(4)
O(3)- C(15)-C(7)	114·4(3)	114·0(3)
O(3)-C(16)-C(17)	103·3(4)	103·8(4)
O(3)-C(16)-C(18)	111·7(4)	112·6(4)
O(3)-C(16)- C(19)	108·0(4)	108·0(4)
C(17)- C(16)-C(18)	113·3(5)	111·5(4)
C(17) C(16)-C(19)	110·1(5)	109·0(4)
C(18)- C(16)- C(19)	110·1(4)	111·6(4)
C(6)-C(1)-C(2)-C(3)	37·4(3)	-43·0(3)
C(2)-C(1) C(6)-C(5)	-52·9(3)	54·3(3)
C(10)- C(1)-C(6)-C(7)	-57·2(3)	59·3(3)
C(6)-C(1)-C(10)-C(9)	47·5(3)	53·6(3)
C(2)-C(3)-C(4)-C(5)	-2·9(3)	2·0(3)
C(4)-C(5)-C(6)-C(1)	39·4(3)	-36·7(3)
C(1)- C(6)-C(7)-C(8)	35·3(3)	-35·2(3)
C(6)- C(7)-C(8)-C(9)	-3·6(2)	7·0(2)
C(7)-C(8)-C(9)-C(10)	-7·4(3)	-0·9(2)
C(10)-C(1)-C(2)-C(3)	-88·4(4)	81·6(4)
C(2)-C(1)-C(6)-C(7)	178·5(5)	-177·2(5)
C(2)-C(1)-C(10)-C(9)	172·2(5)	-177·0(5)
C(1)-C(2)-C(3)-C(4)	-10·5(3)	16·1(3)
C(3)-C(4)-C(5)-C(6)	-11·7(3)	8·4(3)
C(4)-C(5)-C(6)-C(7)	165·2(5)	-162·5(5)
C(5)-C(6)-C(7)-C(8)	-93·3(4)	93·2(4)
C(10)- C(1)-C(6)-C(5)	71·4(3)	-69·2(3)
C(8)--C(9)-C(10)-C(1)	-15·0(2)	23·8(3)

Deslongchamps, 1988). We present here the results from the crystallographic study of the bicyclic compound (3) (Fig. 1), undertaken to determine its relative stereochemistry and exact conformation. Compound (3) was prepared through a base-catalyzed (Cs_2CO_3/CH_3CN, 95% yield) double Michael addition reaction between the dienophile (1) and the diene (2), a modified Nazarov's reagent (Nazarov & Zauyalou, 1953). The cyclization gave compound (3) with total control of the relative stereochemistry as shown in Fig. 1.

Experimental. Crystal: $0·25 \times 0·15 \times 0·25$ mm; Enraf–Nonius CAD-4 diffractometer; graphite-monochromatized Cu $K\bar{\alpha}$ radiation; cell parameters were obtained by least-squares procedure on 24 reflections with 2θ angle in the range 80·00–120·00°. The $\theta/2\theta$ scan mode was used for data collection at a

constant scan speed of $4° min^{-1}$. A total of 9192 reflections was collected (7181 independent) up to $2\theta(max.) = 139\cdot6°$, corresponding to $9 \geq h \geq -9$, $14 \geq k \geq 0$, $24 \geq l \geq -24$. 4473 reflections satisfying $I \geq 2\cdot5\sigma(I)$ were considered as observed. No correction was made for absorption. The *NRCVAX* system was used for all calculations (Gabe, Lee & LePage, 1985). The structure was solved by the application of direct methods and refined by full-matrix least squares on F. Anisotropic thermal parameters were refined for non-H atoms. Some H atoms were refined. Weights based on counting statistics were used. The maximum Δ/σ ratio was $0\cdot427$; in the last ΔF map, the deepest hole was $-0\cdot270\,e\,Å^{-3}$ and the highest peak $0\cdot250\,e\,Å^{-3}$.

Discussion. Table 1 gives the final atomic parameters with their B_{eq} values.* Bond lengths, valence angles and selected torsion angles are given in Table 2. Fig. 1 shows the synthesis scheme. A perspective view is depicted in Fig. 2. The asymmetric unit includes two molecules, the conformations of which are slightly different, as can be seen in Table 2. The results from the crystallographic structure determination indicate that (3) has the expected *cis–syn* relative stereochemistry. The *AB* ring junction is *cis* and the C(10)-methyl† is *syn* relative to the C(1)-cyano. In the crystalline structure we observe that the enol form of the

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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 51690 (39 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

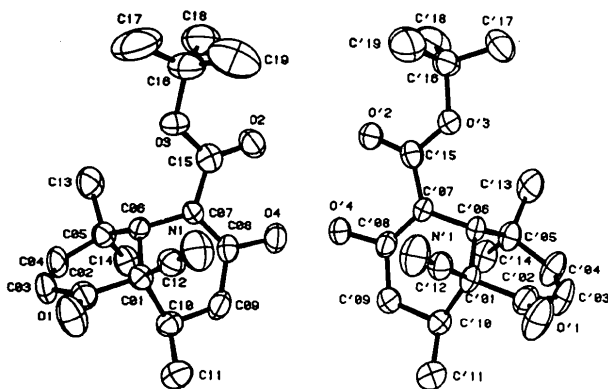† Note that the crystallographic numbering scheme is different from that used to name the compound.

Table 3. *Hydrogen-bond distances* (Å) *and angles* (°) *between donor* (OH) *and acceptor* (O) *atoms*

	O–H···O (°)	O···O (Å)	O–H (Å)	H···O (Å)
Molecule 1				
O(4)–H···O(2)	141 (3)	2·538 (3)	1·12 (3)	1·56 (3)
Molecule 2				
O(4)–H···O(2)	149 (3)	2·582 (4)	1·10 (3)	1·57 (3)

β-ketoester is present in ring B. Table 3 gives the corresponding intramolecular hydrogen-bonding geometry. Even in solution we observe exclusively the enol form in ring B [^{1}H NMR observation of the OH proton of the enol form at 12·9 p.p.m. and ^{13}C NMR observation of the two unsaturated C(7) and C(8) atoms absorbing respectively at 98·4 and 171·2 p.p.m.]. Because of the presence of an enone in ring A and the enol form of the β-ketoester in ring B compound (3) exists with a conformation totally different from that observed for a normal *cis*-decalin (chair conformation). Ring A tends to adopt a planar conformation to reduce the C(1)-cyano and C(10)-methyl steric interaction and ring B exists in a conformation similar to that observed for cyclohexene, with the C(10)-methyl pseudo-equatorial. The relative stereochemistry observed for compound (3) can be explained by taking into account that the formation of this *cis–syn* isomer is produced *via* an *exo* approach of the dienolate ion of (2) to the enone (1) (Berthiaume, Lavallée & Deslongchamps, 1988; Lavallée & Deslongchamps, 1988). The preceding double Michael addition reaction is an example of a new strategy developed for rapid construction of complex organic molecules such as steroids or terpenes. No abnormally short intermolecular contacts were noted in the crystal packing.

Fig. 2. *ORTEP* perspective view and atom numbering.

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