Enamine Chemistry. Part XIX.[1] Stereochemistry of the Transition State of the Reaction of αβ-Unsaturated Acid Chlorides with Enamines: Crystal Structure of 1-Methyl-7-exo-t-butylbicyclo[3.3.1]nonane-2,9-dione

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Treatment of the morpholine enamine of 2-methyl-4-t-butylcyclohexanone with acryloyl chloride in boiling benzene gives 1-methyl-7-t-butylbicyclo[3.3.1]nonane-2,9-dione (VIII) as a mixture of two isomers (4 : 1). X-Ray analysis of the major isomer indicates that initial carbon–carbon bond formation occurs predominantly from the axial side of the enamine double bond. The molecular conformation is boat-chair.

RECENTLY [2] we have provided further evidence to support the contention that N-acylation of the enamine is a necessary prerequisite for the formation of bicyclo-[3.3.1]nonane-2,9-diones in the reaction between αβ-unsaturated acid chlorides and cyclohexanone enamines. The first carbon–carbon bond to be formed in this dione synthesis is that between the β-position of the enamine and the β-position of the acid chloride and the purpose of this investigation was to determine the direction from which this bond formation occurs, in other words whether bond formation is by axial approach from the β-face or equatorial approach † from the α-face.

The reaction between acryloyl chloride and the morpholine enamine of 2-methyl-4-t-butylcyclohexanone has therefore been carried out to give, on mild hydrolysis of the precipitated iminium salt, a 76% yield of 1-methyl-7-t-butylbicyclo[3.3.1]nonane-2,9-dione. The crude product was shown by ^{1}H n.m.r. spectroscopy to consist of two isomers, in the ratio of 4 : 1. The minor component was removed by one crystallisation from benzene–light petroleum and the crystals of the major component were subjected to X-ray analysis (see Experimental section). This showed that the cyclohexanedione ring of the major product had a boat conformation and that the t-butylcyclohexanone ring had a chair conformation [as in (VIII)]. The relevant mechanistic implications of this result are summarised in Scheme 1.

From the work of Johnson [3] the equilibrium isomeric composition of the morpholine enamine of 2-methyl-4-t-butylcyclohexanone is known to be as shown in Scheme 1. The two reactive forms of the enamine [(I) and (III)] equilibrate in the presence of acid through the relatively unreactive form (II) with a more highly substituted double bond. Since in the reaction with an acid chloride, hydrogen chloride is bound to be present, the equilibrium can be maintained as one isomer or the other undergoes reaction.

The X-ray data indicate that the majority of the reaction has occurred by axial attack on the enamine double bond to give (VIII) by paths (A) or (C). Path (C), involving axial attack on the quasi-equatorial orientated methyl enamine (III) can be ruled out since the transition

state is destabilised by developing severe $A^{1,3}$ interactions,[4] as shown in (VI). This is therefore a high-energy process, as is axial attack on the more substituted isomer (II), and can only take place when axial attack on the quasi-axial orientated methyl enamine (I) [path (A)] is rendered reversible, as in the special case of reaction with electrophilic olefins in aprotic non-polar solvents.[5] Although the transition state involved in path (A) is destabilised by the developing 1,3-diaxial interactions leading to (IV), these interactions are considerably smaller ‡ than the $A^{1,3}$ interactions involved in path (C). We therefore conclude that at least 80% of the reaction proceeds by axial attack on (I), the detailed course of the reaction being summarised in Scheme 2.

For cyclisation to the dione to occur the enamine system has to be regenerated [as in (XI)]. However deprotonation of (IV) is stereoelectronically unfavourable, since the equatorial C–H orbital is virtually othogonal to the p orbitals of the iminium group, and orbital overlap will be minimal. If, however, the iminium salt adopts a twist conformation (X), deprotonation can then occur under conditions of stereoelectronic control. Cyclisation of the regenerated enamine double bond on the keten residue gives an enolate anion (XII), evidence for the intermediacy of which in related systems has already been reported.[1]

We have been unable to isolate a pure sample of the minor component detected in the crude 1-methyl-7-t-butylbicyclo[3.3.1]nonane-2,9-dione, but spectroscopic and chemical evidence indicate it to be the other conformational isomer (IX), rather than the structural isomer (XIII) which would arise by reaction of acryloyl chloride with the less reactive enamine (II). Hydrolysis of the mixture gave only the one acid (XIV), whereas (XV) would be formed by ring opening of (XIII). It is difficult to decide whether (IX) would be expected to arise from equatorial attack on (I) [path (B)] or equatorial attack on (III) [path (D)] since although path (B) appears to be ruled out by developing $A^{1,3}$ interactions, these interactions could be eliminated if the iminium salt

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† Approach from underneath the molecule, but still in the plane of the p orbitals of the double bond, leading to a boat or twist conformation of the cyclohexane ring under conditions of stereoelectronic control.

‡ Allinger and Miller [6] have found the energy of a 1,3-diaxial methyl–methyl interaction to be 3·7 kcal mol⁻¹, whereas $A^{1,3}$ methyl–methyl interactions are in the order of 5—6 kcal mol⁻¹.[3]

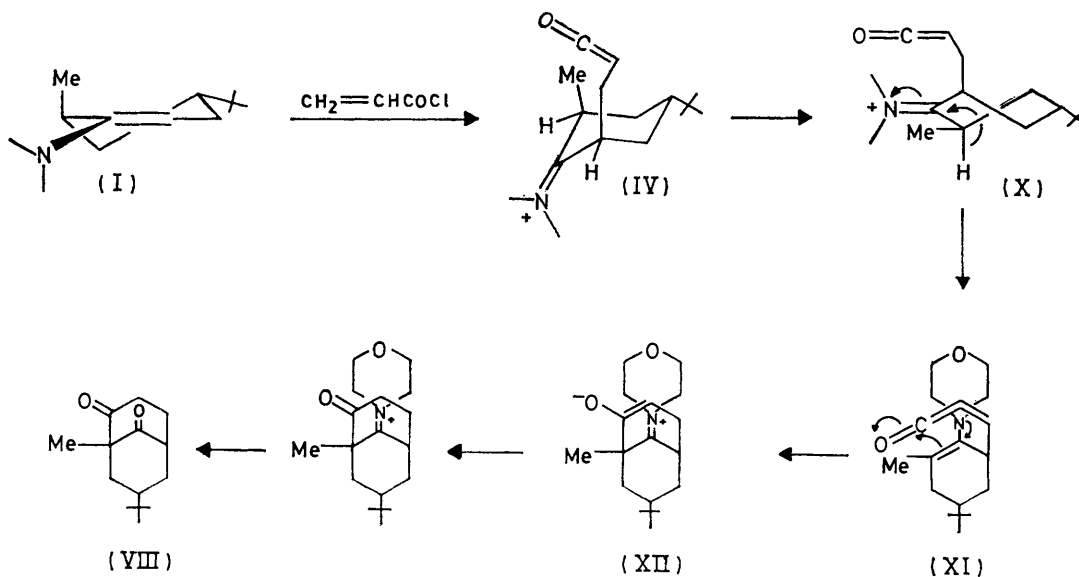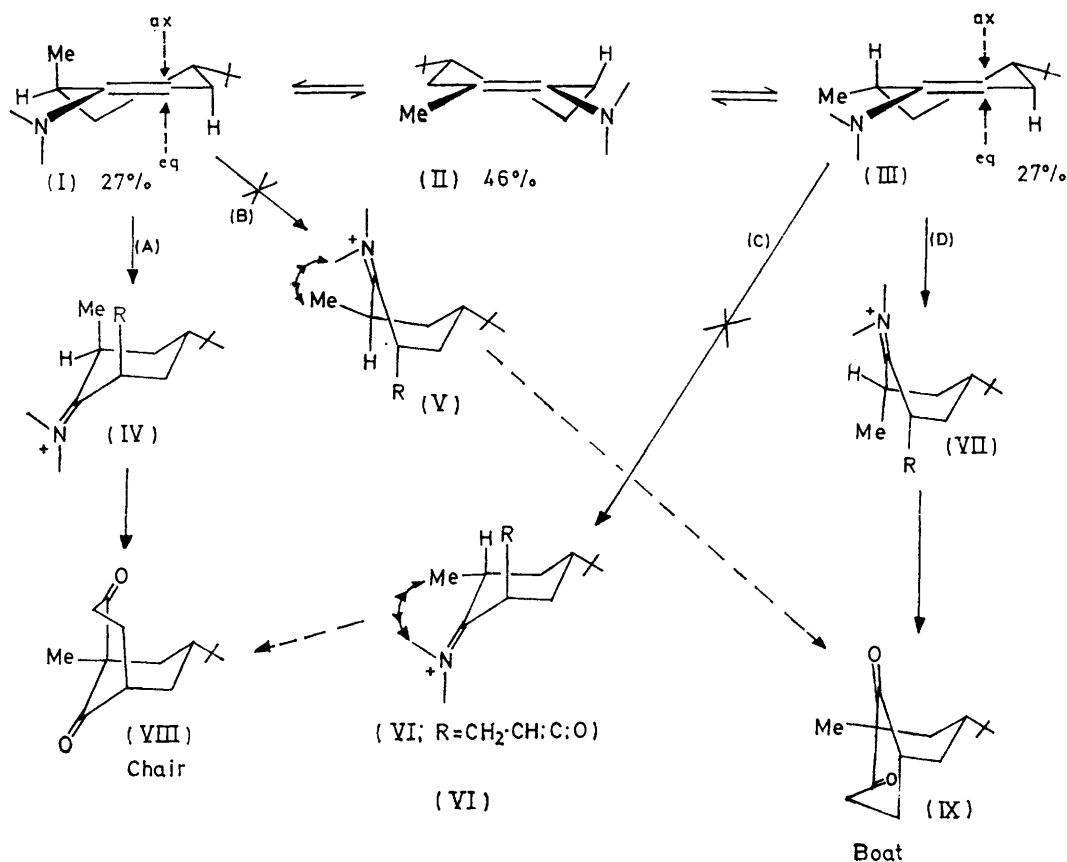[1] P. W. Hickmott, H. Suschitzky and R. Urbani, J.C.S. Perkin I, 1973, 2063.

[2] P. W. Hickmott, G. J. Miles, G. Sheppard, R. Urbani, and C. T. Yoxall, J.C.S. Perkin I, 1973, 1514.

[3] F. Johnson, Internat. Symposium Enamine Chem., Salford, 1969.

[4] F. Johnson, Chem. Rev., 1968, 68, 375.

[5] N. F. Firrell and P. W. Hickmott, Chem. Comm., 1969, 544.

[6] N. L. Allinger and M. A. Miller, J. Amer. Chem. Soc., 1961 83, 2145.

SCHEME 1

SCHEME 2

adopts a twist- instead of the boat-conformation shown in (V).

These results are in general agreement with previous alkylation studies. It has been shown that alkylation of the pyrrolidine enamine of 4-t-butylcyclohexanone occurs predominantly from the axial direction.[7] Our results show that axial approach is still favoured even

when there is an axially orientated 2-substituent present. This does not mean that axial attack by alkylating or acylating agents will always occur. More distant substituents (for example an axial substituent at C-4 of a cyclohexanone ring) which do not give rise to developing

[7] S. Karady, M. Lenfant, and R. E. Wolff, *Bull. Soc. chim. France*, 1965, 2472.

$A^{1,3}$ interactions in the transition state of the enamine reaction could cause preferential attack from the equatorial side, and in fact examples in this category have been reported.[8,9]

Several bicyclo[3.3.1]nonanes lacking substituents at positions 3 and 7 have been shown by X-ray crystallographic studies to adopt a twin-chair conformation in which the cyclohexane rings are distinctly flattened, with the ring valency angles at positions 2, 3, 4, 6, 7, and 8 enlarged by *ca.* 4° beyond the ideal tetrahedral value.[10-12] On the other hand, molecules with a bulky *endo*-substituent at position 3 or 7 evade the severe 3,7-repulsion which would then arise in the twin-chair conformation by adopting the alternative boat-chair conformation.[13,14] The choice of the boat-chair conformation (VIII) is at
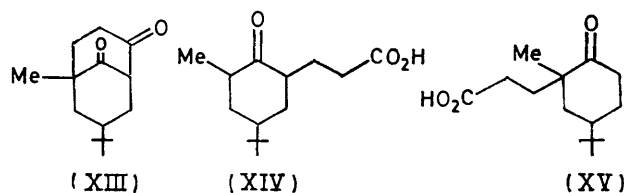
first sight surprising, since this molecule has only hydrogen atoms in the *endo*-positions at C(3) and C(7). However, though cyclohexanones generally adopt the chair conformation,[15,16] the enthalpy difference between chair and twist boat forms of cyclohexanone is *ca.* half that appropriate to cyclohexane and several steroids have boat-like cyclohexanone rings when the alternative chair form would suffer from 1,3-diaxial repulsions; [17] indeed, the preferred conformation of cyclohexane-1,4-dione at normal temperatures is a skew-boat form.[18] Moreover, the flattening of the rings in a twin-chair bicyclo[3.3.1]-nonane results in an *exo*-substituent at position 3 or 7 being no longer purely equatorial in character and the axial-equatorial energy difference in favour of the equatorial orientation of the t-butyl group on a cyclo-hexane ring is very large. The buttressing effect of the bulky t-butyl group would be expected to push the C(7) hydrogen further into the ring and thus increase the C(3) · · · C(7) transannular H · · · H interaction in the twin-chair conformer, thus favouring the boat-chair conformation.

The molecular structure of (VIII) is shown in the Figure. Table 1 lists final atomic co-ordinates and their standard deviations, Table 2 thermal parameters, Table 3 interatomic distances, Table 4 valency angles, Table 5 torsion angles, and Table 6 displacements of the atoms from various planes in the molecule.

[8] U. K. Pandit and P. Houdewind, Internat. Symposium Ambident Reactivity, Salford, 1973.

[9] M. Forchiassin, C. Russo, and A. Risaliti, *Gazzetta*, 1972, **102**, 607.

[10] W. A. C. Brown, G. Eglinton, J. Martin, W. Parker, and G. A. Sim, *Proc. Chem. Soc.*, 1964, 57; W. A. C. Brown, J. Martin, and G. A. Sim, *J. Chem. Soc.*, 1965, 1844.

[11] N. C. Webb and M. R. Becker, *J. Chem. Soc. (B)*, 1967, 1317.

[12] M. Dobler and J. D. Dunitz, *Helv. Chim. Acta*, 1964, **47**, 695.

[13] P. D. Cradwick and G. A. Sim, *J. Chem. Soc. (B)*, 1971, 2218.

[14] C. Tamura and G. A. Sim, *J. Chem. Soc. (B)*, 1968, 1241.

[15] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, ' Conformational Analysis,' Wiley, New York, 1965.

In the cyclohexane-1,3-dione ring atoms C(3) and C(9) are displaced by 0·54 and 0·67 Å to the same side of the
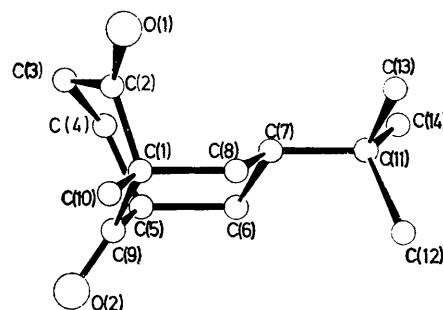
Molecular structure of (VIII), showing the numbering system used in the crystallographic analysis

least-squares plane (*a*) (Table 6). In the other ring atoms C(7) and C(9) are displaced to opposite sides of

TABLE 1

Fractional atomic co-ordinates, with standard deviations in parentheses

	x	*y*	*z*
C(1)	0·2100(4)	0·0747(3)	0·3127(3)
C(2)	0·1104(4)	0·1253(3)	0·1870(3)
C(3)	0·2421(5)	0·1490(4)	0·0860(4)
C(4)	0·4134(5)	0·2206(4)	0·1925(4)
C(5)	0·5063(4)	0·1784(3)	0·3305(4)
C(6)	0·4639(4)	0·2781(4)	0·5057(4)
C(7)	0·2474(4)	0·3029(3)	0·5339(3)
C(8)	0·1674(4)	0·1763(3)	0·4885(3)
C(9)	0·4296(4)	0·0583(3)	0·3039(4)
C(10)	0·1318(7)	−0·0500(4)	0·2796(5)
C(11)	0·2031(5)	0·4041(3)	0·7101(4)
C(12)	0·3016(9)	0·3638(5)	0·8455(5)
C(13)	−0·0181(7)	0·4279(6)	0·7223(6)
C(14)	0·2734(11)	0·5302(4)	0·7408(7)
O(1)	−0·0643(3)	0·1432(2)	0·1683(3)
O(2)	0·5290(4)	−0·0414(2)	0·2791(3)
H(3a)	0·161(5)	0·193(3)	0·022(4)
H(3b)	0·290(5)	0·058(3)	0·006(4)
H(4a)	0·370(5)	0·314(3)	0·244(4)
H(4b)	0·508(5)	0·211(3)	0·119(5)
H(5)	0·646(5)	0·162(3)	0·330(4)
H(6a)	0·510(5)	0·360(3)	0·520(4)
H(6b)	0·537(5)	0·242(3)	0·593(5)
H(7)	0·175(4)	0·338(2)	0·452(3)
H(8a)	0·023(5)	0·191(3)	0·491(4)
H(8b)	0·229(4)	0·140(3)	0·565(4)
H(10a)	0·195(6)	−0·080(4)	0·369(5)
H(10b)	0·168(5)	−0·119(4)	0·167(5)
H(10c)	−0·013(8)	−0·027(4)	0·282(6)
H(12a)	0·431(9)	0·345(6)	0·839(8)
H(12b)	0·271(8)	0·280(6)	0·833(6)
H(12c)	0·277(6)	0·432(4)	0·958(6)
H(13a)	−0·092(8)	0·446(5)	0·620(7)
H(13b)	−0·047(6)	0·506(4)	0·827(5)
H(13c)	−0·050(8)	0·353(5)	0·729(7)
H(14a)	0·225(8)	0·559(5)	0·649(7)
H(14b)	0·415(8)	0·518(5)	0·753(6)
H(14c)	0·235(6)	0·600(4)	0·851(6)

plane (*b*) by 0·65 and 0·70 Å. These displacements are similar to those in the boat-chair molecules 9-benzoyl-3α-

[16] J. B. Lambert, R. E. Carhart, and P. W. R. Corfield, *J. Amer. Chem. Soc.*, 1969, **91**, 3567.

[17] *E.g.* D. H. R. Barton, D. A. Lewis, and J. F. McGhie, *J. Chem. Soc.*, 1957, 2907; J. Levisalles, *Bull. Soc. chim. France*, 1960, 551; M. Balasubramanian, *Chem. Rev.*, 1962, **62**, 591; D. H. R. Barton and G. A. Morrison, *Progr. Org. Chem. Prod.*, 1961, **19**, 165.

[18] N. L. Allinger, H. M. Blatter, L. A. Frieberg, and F. M. Karkowski, *J. Amer. Chem. Soc.*, 1966, **88**, 2999, and references therein.

TABLE 2

(a) Anisotropic thermal parameters ($b_{ij} \times 10^4$) *

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	178(6)	77(3)	127(4)	−15(3)	28(4)	43(3)
C(2)	179(6)	80(3)	109(4)	−24(3)	22(4)	34(3)
C(3)	224(8)	152(5)	145(5)	−60(5)	16(5)	83(4)
C(4)	219(8)	146(5)	180(6)	−54(5)	65(6)	70(4)
C(5)	124(6)	141(4)	168(6)	−19(4)	38(4)	47(4)
C(6)	171(7)	121(4)	171(6)	−45(4)	7(5)	44(4)
C(7)	172(6)	85(3)	118(4)	−17(3)	22(4)	41(3)
C(8)	170(6)	94(3)	123(4)	−20(3)	35(4)	47(3)
C(9)	187(7)	109(3)	124(5)	12(4)	31(4)	41(3)
C(10)	358(11)	95(4)	178(7)	−55(5)	4(7)	58(4)
C(11)	270(8)	94(3)	131(5)	−10(4)	29(5)	31(3)
C(12)	520(19)	152(6)	123(6)	9(8)	26(8)	50(5)
C(13)	311(12)	190(7)	221(9)	41(7)	119(8)	19(7)
C(14)	656(24)	87(4)	223(9)	−63(8)	51(12)	12(5)
O(1)	154(5)	155(3)	180(4)	−16(3)	13(3)	78(3)
O(2)	291(6)	137(3)	247(5)	78(4)	66(5)	69(3)

(b) Isotropic thermal parameters ($B/\text{Å}^2$)

H(3a)	2·5(7)	H(3b)	2·5(7)	H(4a)	2·0(7)
H(4b)	3·3(8)	H(5)	3·2(8)	H(6a)	3·0(8)
H(6b)	3·5(8)	H(7)	0·6(5)	H(8a)	1·8(6)
H(8b)	1·6(6)	H(10a)	4·5(9)	H(10b)	3·3(8)
H(10c)	6·3(13)	H(12a)	8·6(11)	H(12b)	7·1(10)
H(12c)	4·9(10)	H(13a)	7·1(14)	H(13b)	4·2(9)
H(13c)	7·2(16)	H(14a)	8·3(16)	H(14b)	10·9(15)
H(14c)	4·9(10)				

* Anisotropic temperature factors are of the form: $T = \exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)]$.

TABLE 3

(a) Intramolecular distances (Å)

C(1)−C(2)	1·526(4)	C(11)−C(12)	1·525(5)
C(1)−C(10)	1·533(4)	C(11)−C(13)	1·533(5)
C(1)−C(9)	1·520(4)	C(11)−C(14)	1·530(5)
C(2)−C(3)	1·512(4)	C(2)−O(1)	1·201(3)
C(3)−C(4)	1·527(4)	C(9)−O(2)	1·209(3)
C(4)−C(5)	1·548(5)	C(3) · · · C(9)	2·70
C(5)−C(6)	1·540(4)	C(7) · · · C(9)	2·93
C(5)−C(9)	1·495(5)	C(3) · · · C(7)	3·63
C(6)−C(7)	1·526(4)	C(1) · · · C(4)	2·98
C(7)−C(8)	1·534(4)	C(1) · · · C(6)	2·95
C(7)−C(11)	1·555(4)	C(5) · · · C(2)	2·91
C(8)−C(1)	1·551(4)	C(5) · · · C(8)	2·93

(b) Intermolecular distances (<3·90 Å)

O(1) · · · C(4$^{\text{I}}$)	3·62	O(1) · · · C(14$^{\text{III}}$)	3·65
O(1) · · · C(5$^{\text{I}}$)	3·40	O(2) · · · C(3$^{\text{IV}}$)	3·49
O(1) · · · O(1$^{\text{I}}$)	3·51	O(2) · · · C(4$^{\text{IV}}$)	3·88
O(1) · · · C(2$^{\text{I}}$)	3·40	O(2) · · · O(2$^{\text{V}}$)	3·73
O(1) · · · C(3$^{\text{I}}$)	3·50	O(2) · · · C(8$^{\text{V}}$)	3·44
O(1) · · · C(10$^{\text{I}}$)	3·67	O(2) · · · C(12$^{\text{V}}$)	3·50
C(2) · · · C(2$^{\text{I}}$)	3·70	C(4) · · · C(14$^{\text{VI}}$)	3·71
C(3) · · · C(10$^{\text{II}}$)	3·75		

Roman numerals as superscripts refer to the following transformations of the atomic co-ordinates:

I	$1 - x, y, z$	IV	$1 - x, -y, -z$
II	$-x, -y, -z$	V	$1 - x, -y, 1 - z$
III	$-x, 1 - y, 1 - z$	VI	$1 - x, 1 - y, 1 - z$

TABLE 4

Valency angles (deg.)

C(2)−C(1)−C(8)	108·3(2)	C(5)−C(5)−C(7)	113·1(2)
C(2)−C(1)−C(9)	108·9(2)	C(6)−C(7)−C(8)	109·4(3)
C(2)−C(1)−C(10)	110·0(2)	C(6)−C(7)−C(11)	113·5(2)
C(8)−C(1)−C(9)	107·2(2)	C(8)−C(7)−C(11)	113·0(2)
C(8)−C(1)−C(10)	110·2(3)	C(7)−C(8)−C(1)	113·5(2)
C(9)−C(1)−C(10)	112·2(3)	C(1)−C(9)−C(5)	112·5(3)
C(1)−C(2)−C(3)	116·7(2)	C(1)−C(9)−O(2)	122·9(2)
C(1)−C(2)−O(1)	121·2(2)	C(5)−C(9)−O(2)	124·6(3)
C(3)−C(2)−O(1)	122·0(3)	C(7)−C(11)−C(12)	112·4(3)
C(2)−C(3)−C(4)	112·3(2)	C(7)−C(11)−C(13)	109·4(3)
C(3)−C(4)−C(5)	114·6(3)	C(7)−C(11)−C(14)	109·9(3)
C(4)−C(5)−C(6)	113·3(2)	C(12)−C(11)−C(13)	109·3(3)
C(4)−C(5)−C(9)	109·6(2)	C(12)−C(11)−C(14)	108·5(4)
C(6)−C(5)−C(9)	107·9(3)	C(13)−C(11)−C(14)	107·3(4)

TABLE 5

Torsion angles (deg.); standard deviations are ca. 0·4°

C(9)−C(1)−C(2)−C(3)	−0·6	C(7)−C(8)−C(1)−C(9)	55·7
C(8)−C(1)−C(2)−C(3)	115·6	C(7)−C(8)−C(1)−C(10)	178·0
C(10)−C(1)−C(2)−C(3)	−123·9	C(2)−C(1)−C(9)−C(5)	56·1
C(9)−C(1)−C(2)−O(1)	178·3	C(2)−C(1)−C(9)−O(2)	−124·4
C(8)−C(1)−C(2)−O(1)	−65·5	C(8)−C(1)−C(9)−C(5)	−60·9
C(10)−C(1)−C(2)−O(1)	55·0	C(8)−C(1)−C(9)−O(2)	118·7
C(1)−C(2)−C(3)−C(4)	−46·3	C(10)−C(1)−C(9)−C(5)	178·1
O(1)−C(2)−C(3)−C(4)	134·9	C(10)−C(1)−C(9)−O(2)	−2·3
C(2)−C(3)−C(4)−C(5)	40·0	C(4)−C(5)−C(9)−C(1)	−61·8
C(3)−C(4)−C(5)−C(6)	−109·1	C(4)−C(5)−C(9)−O(2)	118·6
C(3)−C(4)−C(5)−C(9)	11·4	C(6)−C(5)−C(9)−C(1)	61·9
C(4)−C(5)−C(6)−C(7)	63·9	C(6)−C(5)−C(9)−O(2)	−117·7
C(9)−C(5)−C(6)−C(7)	−57·6	C(6)−C(7)−C(11)−C(12)	−61·9
C(5)−C(6)−C(7)−C(8)	53·2	C(8)−C(7)−C(11)−C(12)	63·4
C(5)−C(6)−C(7)−C(11)	−179·6	C(6)−C(7)−C(11)−C(13)	176·6
C(6)−C(7)−C(8)−C(1)	−52·7	C(8)−C(7)−C(11)−C(13)	−58·1
C(11)−C(7)−C(8)−C(1)	179·8	C(6)−C(7)−C(11)−C(14)	59·1
C(7)−C(8)−C(1)−C(2)	−61·6	C(8)−C(7)−C(11)−C(14)	−175·6

TABLE 6

Displacements (Å) of the atoms from various planes

Plane (a): C(1), C(2), C(4), C(5)

    C(1) 0·02, C(2) −0·02, C(4) 0·04, C(5) −0·03, C(3) 0·54, C(9) 0·67

Plane (b): C(1), C(5), C(6), C(8)

    C(1) 0, C(5) 0, C(6) 0, C(8) 0, C(7) 0·65, C(9) −0·70

Plane (c): C(3), C(7), C(9)

    O(2) 0·01, C(11) 0·01

bromo-9-azabicyclo[3.3.1]nonan-2-one [13] and 9-benzoyl-3α-bromo-9-azabicyclo[3.3.1]nonan-2β-ol [14] and may be compared with the value of 0·73 Å appropriate to an ideal cyclohexane ring. The mean displacements of C(3) from the 1–2–4–5 and of C(7) from the 1–5–6–8 plane in the twin-chair compounds 1-p-bromophenylsulphonyloxy-methyl-5-methylbicyclo[3.3.1]nonan-9-ol [10] and 2-chloro-bicyclo[3.3.1]nonan-9-one [11] are 0·51 Å. The greater departure from ideal geometry of the rings in the twin-chair bicyclo[3.3.1]nonanes is also reflected in the C(5)–C(6)–C(7)–C(8) and C(1)–C(8)–C(7)–C(6) ring torsion angles which have a mean of only 45° in these twin-chair compounds compared with 53° in the chair ring of (VIII). The C(3) · · · C(9) separation (2·70 Å) in (VIII) may be compared with C(3) · · · N(9) separations (2·61 and 2·56 Å) in 9-benzoyl-3α-bromo-9-azabicyclo[3.3.1]nonan-2-one [13] and 9-benzoyl-3α-bromo-9-azabicyclo[3.3.1]nonan-2β-ol. [14]

EXPERIMENTAL

1-Methyl-7-t-butylbicyclo[3.3.1]nonane-2,9-dione (VIII).—Acryloyl chloride (0·7 ml) in dry benzene (30 ml) was added dropwise to the morpholine enamine of 2-methyl-4-t-butyl-cyclohexanone (2 g) in boiling benzene (50 ml) during 15 min. and the mixture heated under reflux for 4 h. The thick, white precipitate was collected, washed with dry benzene (4 × 20 ml), and hydrolysed by stirring with cold water (40 ml) for 4 h. Extraction with ether gave an oil (1·6 g) which was distilled to give (VIII) (1·42 g, 76%) as a white solid, b.p. 110—115° at 5·35 N m⁻². Recrystallisation (× 2) from 1 : 2 benzene–light petroleum (b.p. 60—80 °C) mixture gave prisms, m.p. 101 °C (Found: C, 75·9; H, 10·2%; M^+, 222. $C_{14}H_{22}O_2$ requires C, 75·6; H, 9·9%; M, 222).

The 60 MHz ^{1}H n.m.r. spectrum (CDCl$_3$) of the crude product obtained after distillation showed a complex methylene envelope at τ 7·7—8·7 and singlets at 8·86 and

9·14 (Me and CMe_3 respectively). At 100 Hz sweepwidth shoulders became apparent on the signals due to the Me and t-butyl groups and on addition of $Eu(fod)_3$ the methyl signal separated into two singlets (ratio 1 : 4). One crystallisation removed the minor component and the mother liquors were evaporated down (to give a mixture of the two isomers *ca.* 1 : 1). The resulting oil was heated under reflux with 1N-sodium hydroxide solution for 30 min, and the solution cooled, extracted with ether, and the aqueous layer acidified with concentrated hydrochloric acid and extracted with ether. The ^1H n.m.r. spectrum with and without the addition of $Eu(fod)_3$ of the crude acid produced showed the methyl signal as a doublet (J 6·5 Hz), as expected for β-(3-methyl-2-oxo-5-t-butylcyclohexyl)propionic acid (XIV); there was no singlet which could be attributed to the presence of any β-(1-methyl-2-oxo-5-t-butylcyclohexyl)propionic acid (XV) which would have been obtained if the crude (VIII) had contained an appreciable amount of the structural isomer (XIII).

Crystal Data.—$C_{14}H_{22}O_2$, $M = 222·3$. Triclinic, $a = 6·962(1)$, $b = 11·730(2)$, $c = 8·990(1)$ Å, $α = 115°$ 36(1)′, $β = 98°$ 23(1)′, $γ = 80°$ 56(1)′, $U = 651·3$ Å³, $Z = 2$, $D_c = 1·13$, $F(000) = 244$, Mo-$K_α$ radiation, $λ = 0·7107$ Å, $μ(Mo-K_α) = 0·80$ cm⁻¹. Space group $P\bar{1}$ (C_i^1).

Crystallographic Measurements.—Preliminary values of the cell dimensions, obtained from rotation and Weissenberg photographs, were adjusted by a least-squares procedure to comply with the θ, χ, and φ setting angles of 12 reflections measured with zirconium-filtered Mo-$K_α$ radiation on a Hilger and Watts Y 290 automatic diffractometer. Intensity measurements were carried out by the θ—2θ step-scan technique, each reflection being scanned over a range of 1·2° in θ with $θ_{calc.}$ at the midpoint of the scan. Each 0·02° step in θ was surveyed for 1 s and background counts were taken at each end of the scan range for 15 s. Two standard reflections were monitored after every 40 intensity measure-

ments and the results used to ensure that all the intensities were on a common scale. Changes in the standard intensities during data collection were small and the crystal showed no sign of decomposition during irradiation. Intensities were collected for reflections with $θ_{calc.}$ ⩽28°. The scan counts P and background counts B_1, B_2 were combined to yield the integrated intensities $I = P - 2(B_1 + B_2)$ which were then corrected for Lorentz and polarisation effects but not for absorption. In all 2733 significant values of $|F_0|$ were derived of which 1680 had $I > 3σ(I)$

Structure Analysis.—The crystal structure was elucidated by the symbolic addition procedure using the ' X-Ray '72 ' series of programmes.[19] Three reflections were given phases of 0° to define the origin and two additional reflections were assigned phases of 0 and 180° in turn. Apart from the trivial case with all phases 0° this gave three possible solutions. One E map had 16 large peaks which corresponded to the 14 carbon and 2 oxygen atoms of the molecule. The initial set of co-ordinates gave R 38·2% and after two cycles of full-matrix least-squares adjustment with isotropic vibration parameters R was 15·1%. When the carbon and oxygen atoms were assigned anisotropic parameters R was lowered to 12·1%.

At this stage the hydrogen atoms apart from the nine hydrogens of the t-butyl group were located from a difference electron-density synthesis and after further refinement a subsequent difference electron-density synthesis revealed the t-butyl hydrogen atoms. Subsequent refinement with anisotropic thermal parameters for the carbon and oxygen atoms and isotropic thermal parameters for the hydrogen atoms led to convergence at R 6·0%. In all these calculations a unit weighting scheme was retained. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21120 (9 pp.).*

[19] ' X-Ray '72 ' system of programs, eds. J. M. Stewart, F. A. Kundell, and J. C. Baldwin, University of Maryland Technical Report, TR 192.

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* See Notice to Authors No. 7 in *J.C.S. Perkin I*, 1973, Index issue.