Crystallographic Studies Related to the Intramolecular Hydride Shift in *exo*-7-Hydroxybicyclo[3.3.1]nonan-3-one

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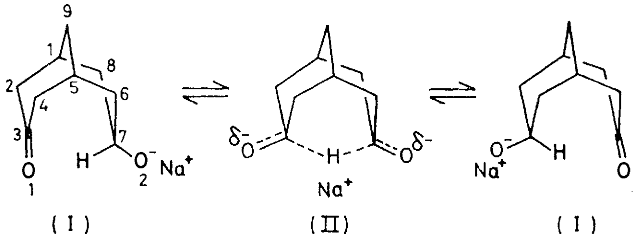
The crystal structure of *exo*-7-hydroxybicyclo[3.3.1]nonan-3-one (III) and *exo*-7-methoxybicyclo[3.3.1]nonan-3-one (IV) have been determined. The structure of (III) shows distortions which may be caused either by partial 3,7-hydride transfer or by a disordered arrangement of undistorted dimers in the crystal. The structure of (IV) shows no unexpected distortions.

In favourable cases, it has been shown [1-8] that distortions in molecular geometry can be regarded as ' frozen-in ' intermediates on a reaction pathway. In general, this occurs when the activation energy for the reaction is not ' too large ' and considerable inter- or intra-molecular forces act to provide the distortion. Most relevant to our system, Bürgi, Dunitz, and Shefter [1,2,4] demonstrated that a complete spectrum of geometries could be found in the crystallographic literature representing the addition of oxygen and nitrogen nucleophiles to carbonyl groups. In addition, they showed [6] that the geometry changes in the reaction were quantitatively similar to those computed *ab initio* for the addition of hydride (H^-) to formaldehyde. The reaction we have studied also involves the formal addition to a carbonyl and should have a similar reaction pathway, which might be observable by determining the crystal structures of suitable model compounds.



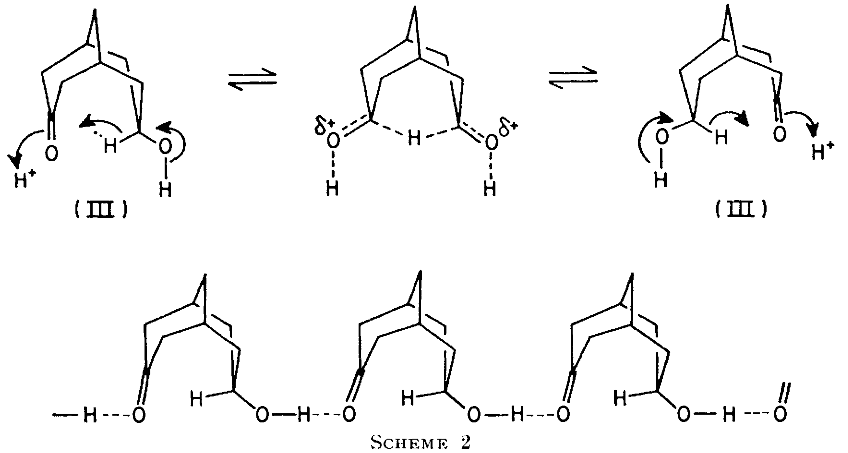
SCHEME 1

We have recently investigated the degenerate rearrangement of the sodium alkoxide (I) by variable-temperature ^1H n.m.r. spectroscopy.[9] It was shown that the reaction involved reversible intramolecular 3,7-hydride transfer, a sequence requiring both expulsion of hydride from alkoxide and delivery of hydride to carbonyl. The degree of concert in these changes remains a matter of conjecture, but microscopic reversibility demands [10] that the reaction pass through a symmetrical transition state (or high-energy intermediate) which we depict as (II).

The activation energy (19.4 kcal mol^{-1} at 113 °C) is still the lowest yet measured for a process of this type,[11] and with this relatively low energy it might be possible for crystal-packing forces in a salt of (I) to freeze out a configuration intermediate between that of (I) and (II).

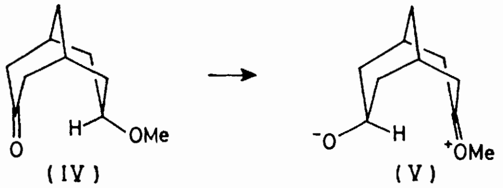
Since we have not yet been able to prepare a crystalline salt of (I), we have studied the protonated form, the parent alcohol (III). 3,7-Hydride transfer could be initiated by proton transfer to the carbonyl group, and, if the proton (H^+) represents the hydroxy-group of a neighbouring molecule, it may be possible to observe partial proton transfer between hydrogen-bonded molecules (see Scheme 2) in the solid state as well as other distortions consistent with motion along the hydride migration pathway. Accordingly the crystal structure of (III) was undertaken.

As a control, we have also investigated the structure of the methyl ether (IV). This compound was prepared by alkylation of the thallium salt of *exo*-7-methylenebicyclo[3.3.1]nonan-3-ol with methyl iodide [12] followed by ozonolytic removal of the methylene group.[13] In (IV) there can be no hydrogen bonding, and the product of



SCHEME 2

hydride shift would be the unstable zwitterion (V), (Scheme 3). It is therefore unlikely that the crystal structure of (IV) will show much distortion along the intramolecular hydride-transfer pathway, whilst significant distortions might be observed in the crystal structure of (III).



SCHEME 3

EXPERIMENTAL

(*a*) *Preparation of Substrates*.—I.r. spectra were recorded on a Perkin-Elmer 457 G spectrophotometer, and n.m.r. spectra with a Perkin-Elmer R 32 spectrometer (90 MHz with tetramethylsilane as internal reference). Mass spectra were determined on an A.E.I. MS 902. Light petroleum refers to the fraction of b.p. 40—60 °C. Silica was silica gel M.F.C. (100—200 mesh). *exo*-7-Hydroxybicyclo-[3.3.1]nonan-3-one was prepared as previously described.[9]

Alkylation of exo-*7-methylenebicyclo*[3.3.1]*nonan-3-ol*. Thallium(I) ethoxide (2.5 g, 0.01 mol) was added to a stirred solution of the alcohol (1.52 g, 0.01 mol) in benzene (60 ml), and the mixture heated and distilled to give 20 ml of distillate. Methyl iodide (3 ml) was then added to the cooled residue and the mixture heated under reflux under a static nitrogen atmosphere for 18 h. Filtration of the heavy orange precipitate and removal of solvent from the filtrate yielded a clear yellow oil which was chromatographed on silica (elution with 50 : 50 v/v ether : light petroleum) to give first the methyl ether (0.88 g, 54%) as a clear colourless oil; $\nu_{max.}$ (CCl_4) 3 069, 2 902, 1 640, 1 445, 1 383, 1 118, 1 097, 908, and 885 cm^{-1}; δ(CCl_4) 0.9—2.4 (12 H, m, unresolved), 3.16 (3 H, s), 3.95 (1 H, t of t, *J* 10.5 and 5.0 Hz), and 4.63 (2 H, s). Further elution gave unreacted alcohol (0.33 g).

exo-*7-Methoxybicyclo*[3.3.1]*nonan-3-one*. Ozone was bubbled into a cooled (−80 °C) solution of the ether (0.72 g) in methanol (50 ml) until a blue colour persisted. Excess of ozone was flushed with nitrogen, then dimethyl sulphide (3 ml) was added and the mixture allowed to warm to room temperature. After 4 h solvent was removed under reduced pressure, and the residue chromatographed on silica (eluting with methylene chloride) to give the methoxyketone (IV) which was recrystallised (0.56 g) from light petroleum; m.p. 85—86 °C (M^+ 168.1155. Calc. for $C_{10}H_{16}O_2$ 168.1151); $\nu_{max.}$ (CCl_4) 2 902, 1 712, 1 409, 1 344, 1 180, 1 151, 1 119, and 1 099 cm.$^{-1}$; δ(CCl_4) 1.1—2.6 (12 H, unresolved), and 3.21 (3 H, s) superimposed on 3.20 (1 H, t of t, *J* 10.5 and 5 Hz).

(*b*) *Crystallography*. (i) *7-Hydroxybicyclo*[3.3.1]*nonan-3-one*. *Crystal data* for (III). $C_9H_{14}O_2$, M_r = 154.20, Monoclinic, a = 13.71(1), b = 7.00(1), c = 8.73(1) Å, β = 80.65(1)° from diffractometer measurements, U = 826.6 Å^3, Z = 4, D_c = 1.239 g cm^{-3}. Mo-K_α radiation, λ = 0.710 7 Å; μ(Mo-K_α) = 0.5 cm^{-1}. Space group $P2_1/a$ (No. 14).

Well-formed crystals of (III) were obtained from diethyl ether. Data were collected from a crystal 0.35 × 0.43 × 0.13 mm for the layers $h0$—$6l$ with $\theta_{max.}$ 27.5° on a Stoe STADI 2 two-circle diffractometer with graphite monochromated Mo-$K_{\bar{\alpha}}$ radiation. This gave 1 376 data of which 990 had $I > 3\sigma(I)$. Lorentz and polarisation corrections (but none for absorption) were applied and the structure solved by direct methods with the SHELX system of programs.[14] Scattering factors were taken from ref. 15. Eleven strong peaks corresponding to atom positions in formula (III) were observed and the structure refined by full-matrix least squares with unit weights. A difference map clearly revealed all the hydrogen atom positions, including that in the hydroxy-group. Heavier atoms were given anisotropic temperature factors, hydrogen atoms were given individual isotropic temperature factors, and refinement was continued, the weighting scheme being: $w = 1/[\sigma^2(F) + 0.000\,6F^2]$.

Convergence was reached with a conventional R factor of 0.049 9. At this stage there were no unusual temperature factors, the highest being for the hydrogen atoms attached to the hydroxy [H(7B) 0.11 Å^2] and to C(7) [H(7A1) 0.09 Å^2]. An analysis of thermal parameters in terms of rigid-body motion showed good agreement (R 0.15) but slight discrepancies for O(2), C(3), and C(7).

However, because of some slightly unusual bond lengths (see Discussion section) this structure was not felt to be totally satisfactory and accordingly no parameters are tabulated. A difference map was calculated and showed several unusual features. The highest peak (P1; 0.36 e Å^{-3}) was 0.93 Å from C(3), the vector C(3) · · · P1 being almost perpendicular to the carbonyl plane. The second-highest peak (P2; 0.17 e Å^{-3}) was 0.82 Å from C(7), and on the opposite side from its attached hydrogen H(7A). The third-largest peak (0.16 e Å^{-3}), lay half-way along the C(4)–C(5) bond, corresponding to normal residual bonding electron density. The next three highest peaks (0.12 e Å^{-3}) were on the periphery of the molecule and had no obvious explanation. The seventh peak (P7; 0.11 e Å^{-3}) lay 0.93 Å from O(1) along the intermolecular O(2) · · · O(1) vector. The largest negative peak (N1; −0.22 e Å^{-3}) lay *ca.* 0.9 Å from C(3) almost diametrically opposite P1. Similarly, though it was less marked, there was a negative region N2 (−0.10 e Å^{-3}) on the opposite side of C(7) to H(7A).

For reasons given in the Discussion section the structure was thought to be disordered and the hydrogen atoms were remodelled. A hydrogen atom H(3A) with occupancy n was located at P1 and H(7A) was given an occupancy $1 - n$. Similarly, an atom H(3B) was introduced at P7 with occupancy n; the occupancy of H(7B) was altered to $1 - n$. Atoms H(3A) and H(7A) were given identical isotropic temperature factors as were H(3B) and H(7B) and n was refined. With these additional parameters the conventional R factor dropped to 0.043 2; R_{155}/R_{162} was 1.155. For an increase in the dimensionality of the problem from 155 to 162 a change in the ratio of R factors by 1.009 would be significant at the 99.5% confidence level.[16] A difference map showed no signs of P1 and a reduced height for P2. There were additional small features in the region of the disorder, but they did not obviously lead to a refinement of the model. Atom parameters * for this structure are given in Table 1, bond lengths in Table 2, bond angles in Table 3, and torsion angles in Table 4.

(ii) *7-Methoxybicyclo*[3.3.1]*nonan-3-one* (IV). Crystals were obtained from light petroleum but, although well-

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* Tables of structure factors for (III) and (IV) together with thermal parameters for (III) are listed in Supplementary Publication No. SUP 22571 (14 pp.). For details see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1978, Index issue.

TABLE 1

Fractional atom co-ordinates ($\times 10^3$) for (III), with estimated standard deviations in parentheses

	x/a	*y/b*	*z/c*	Occupancy
O(2)	9 098(1)	0 357(3)	7 324(2)	
O(1)	11 147(1)	3 096(3)	10 860(2)	
C(1)	11 859(2)	0 653(3)	7 131(3)	
C(8)	10 858(2)	−0 255(3)	7 050(3)	
C(7)	10 002(2)	1 123(3)	7 488(3)	
C(6)	10 168(2)	3 008(4)	6 629(3)	
C(5)	11 181(2)	3 858(3)	6 709(3)	
C(4)	11 292(2)	4 487(3)	8 358(3)	
C(3)	11 399(2)	2 890(4)	9 434(3)	
C(2)	11 988(2)	1 194(4)	8 787(3)	
C(9)	11 989(2)	2 427(4)	6 109(3)	
H(1A)	12 381(19)	−0 287(35)	6 757(28)	
H(8A)	10 742(18)	−1 381(39)	7 724(29)	
H(8B)	10 836(19)	−0 693(36)	6 001(32)	
H(7A)	9 993(21)	1 445(40)	8 889(34)	5 351(223)
N(7B)	8 949(30)	−0 752(67)	7 908(50)	5 351(223)
N(6A)	9 687(20)	3 827(39)	7 020(29)	
H(6B)	10 113(17)	2 829(33)	5 509(29)	
H(5A)	11 234(19)	5 027(35)	6 082(28)	
H(4A)	10 791(18)	5 321(34)	8 815(27)	
H(4B)	11 891(22)	5 195(40)	8 322(30)	
H(3A)	10 815(31)	2 282(52)	9 527(43)	4 649(223)
H(3B)	11 211(43)	2 285(83)	11 280(69)	4 649(223)
H(2A)	12 670(20)	1 544(35)	8 765(28)	
H(2B)	11 815(19)	0 121(32)	9 506(28)	
H(9A)	12 648(21)	2 986(35)	6 135(28)	
H(9B)	11 952(18)	2 099(32)	5 039(30)	

TABLE 2

Bond distances (Å) for (III), with estimated standard deviations in parentheses

O(2)–C(7)	1.379(3)	C(7)–C(6)	1.516(3)
O(1)–C(3)	1.245(3)	C(6)–C(5)	1.524(3)
C(1)–C(8)	1.525(3)	C(5)–C(4)	1.536(3)
C(1)–C(2)	1.532(3)	C(5)–C(9)	1.522(3)
C(1)–C(9)	1.522(3)	C(4)–C(3)	1.483(3)
C(7)–C(8)	1.520(4)	C(3)–C(2)	1.494(3)
O(2)–H(7B)	0.933(49)	C(5)–H(5A)	0.981(25)
O(1)–H(3B)	0.689(60)	C(4)–H(4A)	0.939(26)
C(1)–H(1A)	0.988(25)	C(4)–H(4B)	0.956(29)
C(8)–H(8A)	0.982(28)	C(3)–H(3A)	0.899(42)
C(8)–H(8B)	0.970(27)	C(2)–H(2A)	0.964(27)
C(7)–H(7A)	1.242(30)	C(2)–H(2B)	0.982(24)
C(6)–H(6A)	0.989(28)	C(9)–H(9A)	0.988(27)
C(6)–H(6B)	1.000(24)	C(9)–H(9B)	0.971(25)

formed, they sublimed quickly in the *X*-ray beam. Accordingly they were sealed in a Lindemann glass capillary.

Crystal data for (IV). $C_{10}H_{16}O_2$, $M_r = 166.22$. Monoclinic, $a = 14.78(1)$, $b = 6.114(5)$, $c = 11.52(1)$ Å, $\beta = 115.44(1)°$, from diffractometer measurements, $U = 940.6$ Å^3, $Z = 4$, $D_c = 1.19$ g cm^{-3}. $\mu(\text{Mo-}K_{\bar{\alpha}}) = 0.46$ cm^{-1}. Space group $P2_1/n$ (No. 14).

Data were collected as described for (III) from a crystal 0.3 × 0.25 × 0.25 mm for layers *h*0—5*l* to $\theta_{\text{max.}} \leqslant 23°$. There was no apparent decrease in the intensity of a standard reflexion but many of the data were rather weak with only 682 reflexions out of 1 309 collected having $I > 3\sigma(I)$. Data collection and structure solution were as for (III). All twelve non-hydrogen atoms were located, and refinement proceeded as for (III) with all hydrogen atoms being located and refined. Full-matrix least-squares refinement with anisotropic temperature factors for all non-hydrogen atoms and individual isotropic temperature factors for hydrogens converged at *R* 0.070 with $w = 1/[\sigma^2(F) + 0.002\ F^2]$.

A difference map showed no evidence of the disorder present in (III). Atom parameters are given in Table 5, bond lengths in Table 6, bond angles in Table 7, and torsion

TABLE 3

Bond angles (°) for (III), with estimated standard deviations in parentheses

C(8)–C(1)–C(2)	112.9(2)	H(7A)–C(7)–C(8)	104.3(13)
C(9)–C(1)–C(8)	109.4(2)	H(7A)–C(7)–C(6)	107.8(13)
C(9)–C(1)–C(2)	109.4(2)	H(6A)–C(6)–C(7)	109.0(16)
C(7)–C(8)–C(1)	112.9(2)	H(6A)–C(6)–C(5)	110.6(17)
C(6)–C(7)–O(2)	113.4(2)	H(6B)–C(6)–C(7)	110.2(14)
C(6)–C(7)–O(2)	110.6(2)	H(6B)–C(6)–C(5)	107.9(14)
C(6)–C(7)–C(8)	112.3(2)	H(6B)–C(6)–H(6A)	106.5(21)
C(5)–C(6)–C(7)	112.4(2)	H(5A)–C(5)–C(6)	106.6(15)
C(4)–C(5)–C(6)	112.6(2)	H(5A)–C(5)–C(4)	105.9(14)
C(9)–C(5)–C(6)	110.2(2)	H(5A)–C(5)–C(9)	111.9(14)
C(9)–C(5)–C(4)	109.5(2)	H(4A)–C(4)–C(5)	113.6(14)
C(3)–C(4)–C(5)	114.4(2)	H(4A)–C(4)–C(3)	109.8(14)
C(4)–C(3)–O(1)	120.4(2)	H(4B)–C(4)–C(5)	109.5(16)
C(2)–C(3)–O(1)	121.0(2)	H(4B)–C(4)–C(3)	103.8(17)
C(2)–C(3)–C(4)	117.5(2)	H(4B)–C(4)–H(4A)	104.9(21)
C(3)–C(2)–C(1)	114.5(2)	H(3A)–C(3)–O(1)	82.3(24)
C(5)–C(9)–C(1)	109.0(2)	H(3A)–C(3)–C(4)	103.6(24)
H(7B)–O(2)–C(7)	112.8(25)	H(3A)–C(3)–C(2)	94.4(22)
H(3B)–O(1)–C(3)	113.4(48)	H(2A)–C(2)–C(1)	107.7(14)
H(1A)–C(1)–C(8)	108.4(14)	H(2A)–C(2)–C(3)	105.6(15)
H(1A)–C(1)–C(2)	106.7(15)	H(2B)–C(2)–C(1)	111.2(13)
H(1A)–C(1)–C(9)	109.9(14)	H(2B)–C(2)–C(3)	107.8(13)
H(8A)–C(8)–C(1)	111.4(14)	H(2B)–C(2)–H(2A)	109.9(21)
H(8A)–C(8)–C(3)	108.4(14)	H(9A)–C(9)–C(1)	109.3(15)
H(8B)–C(8)–C(1)	110.0(15)	H(9A)–C(9)–C(5)	110.4(14)
H(8B)–C(8)–C(7)	107.3(15)	H(9B)–C(9)–C(1)	110.6(14)
H(8B)–C(8)–H(8A)	106.6(20)	H(9B)–C(9)–C(5)	109.7(14)
H(7A)–C(7)–O(2)	107.9(13)	H(9B)–C(9)–H(9A)	107.9(20)

TABLE 4

Torsion angles (°) for (III)

C(2)–C(1)–C(8)–C(7)	66.0	C(7)–C(6)–C(5)–C(4)	−66.7
C(9)–C(1)–C(8)–C(7)	−56.0	C(7)–C(6)–C(5)–C(9)	54.5
C(8)–C(1)–C(2)–C(3)	−73.0	C(6)–C(5)–C(4)–C(3)	73.3
C(9)–C(1)–C(2)–C(3)	49.3	C(9)–C(5)–C(4)–C(3)	−49.0
C(8)–C(1)–C(9)–C(5)	60.6	C(6)–C(5)–C(9)–C(1)	−60.0
C(2)–C(1)–C(9)–C(5)	−64.1	C(4)–C(5)–C(9)–C(1)	63.6
C(1)–C(8)–C(7)–O(2)	176.7	C(5)–C(4)–C(3)–O(1)	−152.6
C(1)–C(8)–C(7)–C(6)	50.3	C(5)–C(4)–C(3)–C(2)	36.8
O(2)–C(7)–C(6)–C(5)	−176.8	O(1)–C(3)–C(2)–C(1)	152.8
C(8)–C(7)–C(6)–C(5)	−49.3	C(4)–C(3)–C(2)–C(1)	−36.7

TABLE 5

Fractional atom co-ordinates for (IV) ($\times 10^3$), with estimated standard deviations in parentheses

	x/a	*y/b*	*z/c*
C(1)	7 884(5)	1 635(10)	5 012(7)
C(8)	7 438(6)	0 362(13)	3 758(7)
C(7)	6 316(5)	0 180(10)	3 214(6)
C(6)	5 833(6)	2 397(14)	3 112(7)
C(5)	5 311(6)	3 703(12)	4 370(7)
C(4)	6 097(7)	2 684(16)	5 426(9)
C(3)	6 712(6)	0 661(13)	6 008(6)
C(2)	7 747(7)	0 565(14)	6 103(8)
C(9)	7 433(7)	3 917(14)	4 798(9)
C(10)	5 027(5)	−1 640(18)	1 488(9)
O(2)	6 010(4)	−0 843(8)	1 981(4)
O(2)	6 379(4)	−0 792(9)	6 436(4)
H(1A)	8 602(39)	1 875(81)	5 264(45)
H(8A)	7 640(40)	1 115(97)	3 178(49)
H(8B)	7 697(30)	−0 977(85)	3 946(50)
H(7A)	6 109(28)	−0 856(71)	3 817(39)
H(6A)	5 074(45)	2 310(101)	2 825(52)
H(6B)	5 946(34)	3 066(72)	2 543(44)
H(5A)	5 991(44)	5 083(90)	4 159(55)
H(4A)	5 383(39)	2 208(98)	5 093(49)
H(4B)	6 225(49)	3 623(127)	6 092(64)
H(2A)	8 201(39)	1 330(88)	6 866(50)
H(2B)	7 966(39)	−8 885(83)	6 146(48)
H(9A)	7 717(39)	4 612(84)	5 568(52)
H(9B)	7 551(51)	4 485(116)	4 193(72)
H(10A)	4 932(38)	−2 233(81)	0 813(45)
H(10B)	4 510(103)	−0 527(241)	1 465(145)
H(10C)	4 894(48)	−2 743(110)	2 108(62)

angles in Table 8. Views of the molecules are shown in Figures 1 and 2.

TABLE 6

Bond distances (Å) for (IV), with estimated standard deviations in parentheses

C(1)–C(8)	1.519(8)	C(5)–C(4)	1.516(9)
C(1)–C(2)	1.505(9)	C(5)–C(9)	1.520(10)
C(1)–C(9)	1.520(9)	C(4)–C(3)	1.510(9)
C(8)–C(7)	1.504(8)	C(3)–C(2)	1.488(9)
C(7)–C(6)	1.513(8)	C(3)–O(1)	1.218(7)
C(7)–O(2)	1.435(6)	C(10)–O(2)	1.400(9)
C(6)–C(5)	1.536(9)		
C(1)–H(1A)	0.985(48)	C(4)–H(4B)	0.911(71)
C(8)–H(8A)	0.959(56)	C(2)–H(2A)	0.967(51)
C(8)–H(8B)	0.890(49)	C(2)–H(2B)	0.938(47)
C(7)–H(7A)	1.086(42)	C(9)–H(9A)	0.907(52)
C(6)–H(6A)	1.026(56)	C(9)–H(9B)	0.861(75)
C(6)–H(6B)	0.848(42)	C(10)–H(10A)	0.794(44)
C(5)–H(5A)	0.946(54)	C(10)–H(10B)	1.022(152)
C(4)–H(4A)	1.001(50)	C(10)–H(10C)	1.078(70)

TABLE 7

Bond angles (°) for (IV), with estimated standard deviations in parentheses

C(2)–C(1)–C(8)	114.4(6)	H(6A)–C(6)–C(7)	113.1(37)
C(9)–C(1)–C(8)	109.6(7)	H(6A)–C(6)–C(5)	109.1(34)
C(9)–C(1)–C(2)	109.1(7)	H(6B)–C(6)–C(7)	104.4(32)
C(7)–C(8)–C(1)	112.6(6)	H(6B)–C(6)–C(5)	108.4(33)
C(6)–C(7)–C(8)	111.4(6)	H(6B)–C(6)–H(6A)	109.1(46)
O(1)–C(7)–C(8)	105.6(5)	H(5A)–C(5)–C(6)	104.1(36)
O(1)–C(7)–C(6)	112.1(5)	H(5A)–C(5)–C(6)	108.7(38)
C(5)–C(6)–C(7)	112.5(6)	H(5A)–C(5)–C(9)	111.2(36)
C(4)–C(5)–C(6)	112.0(7)	H(4A)–C(4)–C(5)	111.2(32)
C(9)–C(5)–C(6)	110.3(7)	H(4A)–C(4)–C(3)	105.4(34)
C(9)–C(5)–C(4)	110.4(7)	H(4B)–C(4)–C(5)	112.3(45)
C(3)–C(4)–C(5)	113.6(6)	H(4B)–C(4)–C(3)	106.0(46)
C(2)–C(3)–C(4)	117.9(7)	H(4B)–C(4)–H(4A)	107.9(33)
O(1)–C(3)–C(4)	120.5(7)	H(2A)–C(2)–C(1)	105.0(31)
O(1)–C(3)–C(2)	121.5(8)	H(2A)–C(2)–C(3)	109.8(32)
C(3)–C(2)–C(1)	115.1(7)	H(2B)–C(2)–C(1)	106.7(35)
C(5)–C(9)–C(1)	108.3(7)	H(2B)–C(2)–C(3)	111.2(36)
C(10)–O(2)–C(7)	113.5(6)	H(2B)–C(2)–H(2A)	108.7(48)
H(1A)–C(1)–C(8)	109.2(30)	H(9A)–C(9)–C(1)	106.5(33)
H(1A)–C(1)–C(2)	109.5(29)	H(9A)–C(9)–C(5)	109.8(36)
H(1A)–C(1)–C(9)	104.6(30)	H(9B)–C(9)–C(1)	106.0(48)
H(8A)–C(8)–C(1)	106.3(33)	H(9B)–C(9)–C(5)	110.2(48)
H(8A)–C(8)–C(7)	111.2(33)	H(9B)–C(9)–H(9A)	115.7(60)
H(8B)–C(8)–C(1)	105.9(36)	H(10A)–C(10)–O(2)	106.7(41)
H(8B)–C(8)–C(7)	108.3(36)	H(10B)–C(10)–O(2)	114.1(71)
H(8B)–C(8)–H(8A)	112.5(52)	H(10B)–C(10)–H(10A)	118.3(90)
H(7A)–C(7)–C(8)	110.6(21)	H(10C)–C(10)–O(2)	112.9(34)
H(7A)–C(7)–C(6)	108.2(23)	H(10C)–C(10)–H(10A)	110.8(52)
H(7A)–C(7)–O(2)	108.9(22)	H(10C)–C(10)–H(10B)	93.7(84)

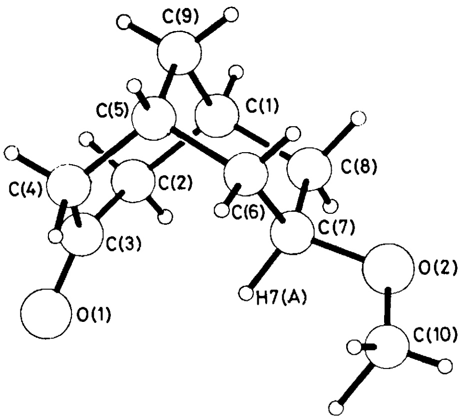


FIGURE 1 A general view of (IV) showing the atom numbering scheme employed for the heavy atoms in both molecules [in (III) the methyl group at C(10) is replaced by H(7B)]

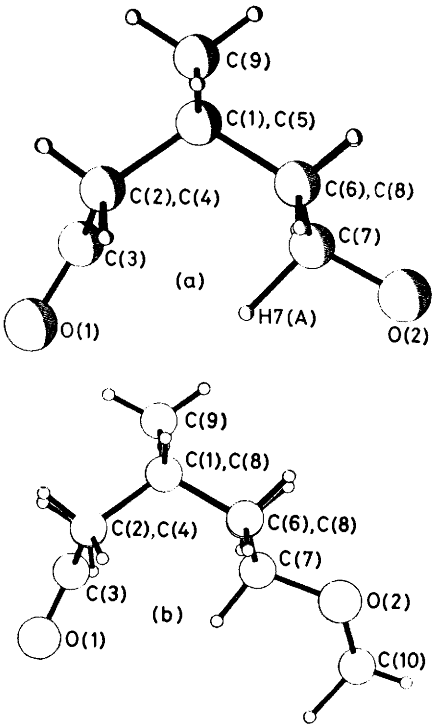


FIGURE 2 Views of (a) (III) and (b) (IV) perpendicular to the approximate mirror plane [of the disordered hydrogen atoms, only H(7A) is shown]

TABLE 8

Torsion angles (°) for (IV)

C(2)–C(1)–C(8)–C(7)	64.5	C(6)–C(7)–O(2)–C(10)	−74.0
C(9)–C(1)–C(8)–C(7)	−59.2	C(7)–C(6)–C(5)–C(4)	−67.5
C(8)–C(1)–C(2)–C(3)	−73.0	C(7)–C(6)–C(5)–C(9)	55.2
C(9)–C(1)–C(2)–C(3)	50.8	C(6)–C(5)–C(6)–C(3)	74.8
C(8)–C(1)–C(9)–C(5)	62.2	C(9)–C(5)–C(6)–C(3)	−48.0
C(2)–C(1)–C(9)–C(5)	−64.6	C(6)–C(5)–C(3)–C(1)	−60.3
C(1)–C(8)–C(7)–C(6)	52.1	C(4)–C(5)–C(9)–C(1)	63.6
C(1)–C(8)–C(7)–O(2)	173.9	C(5)–C(4)–C(3)–C(2)	34.8
C(8)–C(7)–C(6)–C(5)	−50.1	C(5)–C(4)–C(3)–O(1)	−149.8
O(2)–C(7)–C(6)–C(5)	−168.1	C(6)–C(3)–C(2)–C(1)	−36.3
C(8)–C(7)–O(2)–C(10)	165.0	O(1)–C(3)–C(2)–C(1)	148.3

DISCUSSION

Straightforward refinement of (III) yielded an apparently satisfactory and accurate determination of the molecular geometry with the extremely gratifying result that the carbonyl group was markedly non-planar (with the central carbon *ca.* 0.1 Å out of the plane). In addition the C=O bond was *ca.* 0.03 Å longer than for a normal ketone [such as (IV)]. At the other side of the molecule C(7)–O(2) was considerably shorter than a normal single bond and the pyramidality of C(7) somewhat lessened from that of the corresponding group in (IV). The C–H bond lengths fell into a well-defined range (0.90—1.00(3) Å) apart from C(7)–H(7A) which was remarkably long at 1.19 Å, well outside experimental error. There is intermolecular hydrogen bonding between ketone and hydroxy-groups to form a centrosymmetric dimer (Figure 3).

The whole structure looks, at first sight, like an extremely well defined example of distortions caused by partial movement along a reaction pathway. The hydrogen bonding serves to provide a proton source and sink exactly where needed. Even the analysis of thermal parameters (on the assumption of rigid-body motion) fits well, since the only atoms which are inconsistent with this model [C(3), C(7), and O(2)] are just those which might have severe anisotropic motion due to the incipient reaction.

However, the difference map contained small but significant features (described in the Experimental section). In particular, there was an unusual combination of positive and negative peaks flanking both C(3) and C(7). Normally this would signify that these atoms were wrongly placed but it seems unlikely that they are out of position at the convergence of refinement (with a weighting scheme that has been refined). Several points suggested disorder. First, there were possible additional peaks corresponding to hydrogen atoms (though with fractional occupancies). Secondly, the observed difference density can be explained by a combination of overlapping gaussian peaks. We can represent two nearly coincident gaussian peaks with equal half-widths but unequal occupancies *m* and *n* by the expression:

$$m \exp[-(an-x)^2] + n \exp[-(am-x)^2] \qquad (1)$$

which can be rewritten (if second-order terms are neglected) as:

$$k_1 e^{x^{-2}} + k_2 x \,.\, e^{-x^2} \qquad (2)$$

The least-squares process will fit the first term exactly (if necessary by using an unusual temperature factor) but the second, antisymmetric, term cannot be accommodated and will remain; no adjustment of the atomic position can improve the agreement. The difference map is perfectly consistent with the attempt to represent equations (1) or (2) by a single gaussian. Thirdly, the dimer has an almost exact plane of symmetry shown by the dotted line in Figure 3, and because of the lack of severe packing constraints (Table 9) it is possible to substitute some of the dimers with their reflections about this line. Remarkably, almost all the atoms superimpose exactly on each other; the only ones showing any discrepancy being the pairs: C(3), C(7); C(2), C(8); and C(4), C(6). It is quite feasible that the crystal consists of dimers with almost random orientation about the pseudomirror plane and this disorder will mainly be reflected in modified co-ordinates and temperature factors of C(3) and C(7).

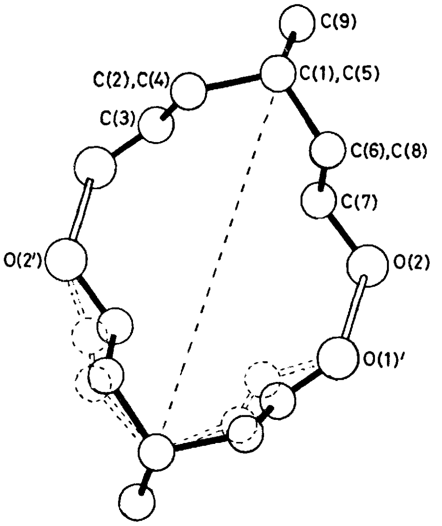


FIGURE 3 A view of the centrosymmetric dimer formed by (III) in the crystal. Full lines correspond to the final parameters; hollow lines represent O(2) · · · O(1) hydrogen bonds. The view is perpendicular to the best least-squares plane through the dimer. Dotted line represents a plane perpendicular to the paper, about which the dimer has approximate mirror symmetry. Dotted bonds and atoms represent the reflection of one molecule in this plane, corresponding to possible disorder of the dimer

TABLE 9

Intermolecular contacts (Å) <3.5 Å

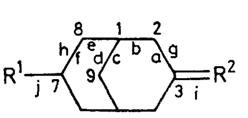
(*a*) In (III)		
	O(2) · · · O(1^{I})	2.879(3)
	C(2) · · · O(1^{II})	3.408(3)
(*b*) In (IV)		
	O(1) · · · C(2^{III})	3.395(7)

Roman numeral superscripts denote the following equivalent positions relative to the reference molecule at *x*, *y*, *z*:

I $2 - x, -y, 2 - z$ III $1\frac{1}{2} - x, y - \frac{1}{2}, 1\frac{1}{2} - z$
II $2\frac{1}{2} - x, y - \frac{1}{2}, 2 - z$

TABLE 10

Comparison of molecular geometry in some bicyclo[3.3.1]-nonane derivatives. Idealized symmetry (C_s or C_{2v}) has been assumed and values averaged where appropriate. Estimated deviations (Å) in bond lengths are 0.003 for (III) and 0.007 for (IV), in torsion angles 0.3° for (III) and 0.6° for (IV)



	R^1	R^2
(III)	OH	O
(IV)	OMe	O
(VI)	H	H_2

(*a*) Bond lengths (Å)

	(III) [a]	(IV) [a]	(III) [b]	(VI)
d	1.488	1.500	1.511	
b	1.534	1.510	1.533	
c	1.522	1.520	1.527	
e	1.525	1.527	1.534	1.536 [d]
f	1.518	1.508	1.529	
i	1.245	1.218	1.224	
j	1.379	1.435	1.429	

(*b*) Torsion angles (°)

	(III) [a]	(IV) [a]	(III) [b]	
d	−36.8	−35.6	−40.7	
b	49.2	49.4	−51.8	
c	−63.8	−64.1	−62.1	
d	60.3	61.2	63.3	
e	−55.2	−57.2	−56.1	−53
f	49.8	51.1	48.7	
g	152.8	149.0	131.4	
h	176.7	171.0	179.0	

(*c*) Displacement (Å) of atoms from mean plane of neighbours

	(III) [a]	(IV) [a]	(III) [b]
C(3)	0.42	0.50	0.57
C(7)	0.09	0.03	0.0

[a] Crystal structure. This work. Final parameters. [b] Calculated using Allinger's 1972 force field. [c] Electron diffraction (ref. 17). [d] Mean.

The crystal structure of (III) is thus consistent both with an intermediate along the reaction pathway for intramolecular hydride transfer and also with a disordered arrangement of essentially undistorted dimers. We cannot distinguish between them on the basis of *X*-ray evidence and, since the distortions expected in (III) due to partial reaction will probably be small, we cannot prove that the unusual geometry is not wholly due to disorder.

By contrast the structure of (IV) is apparently quite normal, although of lower accuracy than that of (III). No significant distortions are present, nor is there any evidence of disorder. In comparing the geometries of (III) and (IV) we have included the results of a force-field calculation on (III) carried out by us with Allinger's 1972 force field.[17] We have also tabulated the geometry of bicyclo[3.3.1]nonane (VI) as determined by electron diffraction.[18] It can be seen that cyclohexane and cyclohexanone rings show good conformational agreement (Table 10) although the effect of distortion (whether due to disorder or reaction) can be seen in the parameters of (III).

Despite the inconclusive results of the present study there is, in principle, no reason why accurate determinations of the structures of molecules such as (III) should not show incipient hydride transfer in the solid state, but it is clear that all possibility of crystallographic artefacts (such as disorder) must be eliminated.

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