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Studies on the Polymerization of Acrolein Oxime. XVI.[†] Structure of 8-Hydroxy-1,4,5,7-tetramethyl-6,8-diazabicyclo[3.2.1]oct-6-ene 6-Oxide

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The thermal oligomerization of 3-methyl-3-buten-2-one oxime leads to crystalline nitrone derivatives, 8-hydroxy-1,4,5,7-tetramethyl-6,8-diazabicyclo[3.2.1]oct-6-ene 6-oxide. Its crystal structure has been determined by X-ray diffraction. The space group is $P2_1/n$ with $a=9.459(3)$, $b=10.335(3)$, $c=11.352(4)$ Å, $\beta=105.50(2)°$, and $Z=4$.

α,β-Unsaturated aldehyde and ketone oximes which have a vinylic double bond conjugated with a C=N double bond are heated to give oligomers. For example, heating of acrylaldehyde oxime leads to an amorphous oligomer with a molecular weight of *ca.* 2000.¹⁾ Methacrylaldehyde oxime is easily converted into the crystalline trimer, 2,4,7-trimethylperhydroisoxazolo[2,3-*a*]pyridine-2,7-dicarbaldehyde dioxime, on heating at 80 °C, but no dimer can be isolated.²⁾ In the course of the study of the polymerization of 3-methyl-3-buten-2-one oxime (MIKOM), it was found that MIKOM gives preferentially the cyclic dimer, 8-hydroxy-1,4,5,7-tetramethyl-6,8-diazabicyclo[3.2.1]-oct-6-ene 6-oxide (**1**). The most plausible reaction mechanism has been reported in the preceding paper;³⁾ *i.e.*, the Diels-Alder reaction must occur first, followed by the Michael addition. Since colorless needle-like crystals of **1** were obtained, the three-dimensional structure of this cyclic dimer was determined by X-ray analysis.

Experimental

Materials and Oligomerization. 3-Methyl-3-buten-2-one was prepared according to the procedure of White,⁴⁾ and then treated with aqueous hydroxylamine hydrochloride to give MIKOM in a 40% yield. Oligomerization of MIKOM was carried out at 80 °C for 375 h in an ampoule. The colorless solution gradually turns yellow with time. After unreacted MIKOM had been removed by distillation under reduced pressure, the residue was treated with a large amount of ether to precipitate the dimer. Yield 12%, IR (KBr): 3150 (OH), 1601 (C=N). Found: C, 60.85; H, 9.33; N, 14.42%. Calcd for $C_{10}H_{18}N_2O_2$: C, 60.58; H, 9.15; N, 14.12%. Recrystallization of the dimer from methanol solution gave colorless needle-like crystals. Mp, 147 °C.

Mass and NMR Measurements. The mass spectra were measured on a Shimadzu LKB-9000 mass spectrometer, equipped with a gaschromatographic inlet system. The ionizing potential was 70 eV, and the ionizing current was 60 μA. The ^{13}C-NMR spectra were obtained with a Hitachi R-42 FT apparatus (22.6 MHz), using DMSO-d_6 as the solvent and the internal standard.

X-Ray Measurements. A crystal of 0.2 mm × 0.2 mm × 0.3 mm in dimensions was used for data collection on a Syntex R-3 automated four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. The accurate unit-cell dimensions were determined by least-squares calculation. The crystal data are summarized in Table 1.

TABLE 1. CRYSTAL DATA

$C_{10}H_{18}N_2O_2$,	M.W.=198.27
Space group	$P2_1/n$
a/Å 9.459(3)	U/Å^3 1069(1)
b/Å 10.335(3)	$Z=4$
c/Å 11.352(4)	D_x/g cm^{-3} 1.23
β/° 105.50(2)	μ(Mo $K\alpha$)/cm^{-1} 0.9

All reflections within the range of $3° \leqq 2\theta \leqq 60°$ were collected by the use of the ω scan mode at a scan speed varying with intensities.⁵⁾ The intensities of three reference reflections were measured periodically; they showed no significant fluctuation during the course of data collection. A total of 3563 independent reflections were collected, among which 1586 reflections with $I \geqq 1.96\sigma(I)$ were used for structure refinement. The intensities were corrected for Lorentz and polarization effects, but not for absorption.

Structure Determination and Refinement. The structure was solved by the direct method and the atomic parameters were refined by the block-diagonal least-squares method. The final R-value for 710 reflections of $F_o \geqq 5$ was 0.083. In the least-squares procedure, the function minimized was $\sum w(|F_o|-|F_c|)^2$, where $w=1$ for 710 reflections of $F_o \geqq 5$ and $w=0$ for the others. The computer programs used were MULTAN program⁶⁾ modified for the Syntex R-3 diffractometer. All the calculations were carried out on a NOVA computer connected to the diffractometer. The atomic scattering factors were taken from "International Tables for X-Ray Crystallography."⁷⁾ The final atomic parameters are given in Table 2. The F_o-F_c table and anisotropic temperature factor table are kept as Document No. 8202 at the Chemical Society of Japan.

Results and Discussion

The bond distances and bond angles are listed in Tables 3 and 4, respectively. The N(6)–C(7)–C(12) and C(7)–N(6)–O(14) angles agree fairly well with those expected from the sp² hybrid orbital. Considerable deviations of the N(6)–C(7)–C(1) and C(7)–N(6)–C(5) angles from the theoretical values for the sp² orbital may be ascribed to the highly-strained ring system. Figure 1 shows the perspective drawing of the molecule and the numbering scheme. It is a bicyclic compound having three rings; the seven-

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[†] Part XV: T. Ota, S. Masuda, and H. Tanaka, *Chem. Lett.*, **1981**, 411.

TABLE 2. ATOMIC CO-ORDINATES, MULTIPLIED BY 10^4 FOE NON-HYDROGEN ATOMS AND BY 10^3 FOR HYDROGEN ATOMS

Atoms	x	y	z	Atoms	x	y	z
O(13)	12490(4)	2570(4)	4367(3)	H(21)	1079(6)	−104(5)	203(5)
O(14)	9092(5)	3139(3)	1572(3)	H(22)	1138(6)	−88(5)	372(5)
N(6)	11477(6)	1458(4)	4071(4)	H(31)	877(5)	2(5)	166(5)
N(8)	10023(5)	2342(4)	2239(4)	H(32)	875(6)	−105(5)	274(5)
C(1)	11752(7)	807(5)	2993(5)	H(4)	921(6)	63(5)	448(5)
C(2)	10894(8)	−476(5)	2887(6)	H(91)	1419(6)	132(5)	309(5)
C(3)	9248(7)	−225(5)	2682(6)	H(92)	1337(5)	−12(5)	240(5)
C(4)	8925(7)	877(5)	3469(5)	H(93)	1393(5)	13(5)	407(5)
C(5)	10019(7)	2012(5)	3547(4)	H(101)	672(6)	43(5)	290(5)
C(7)	11056(6)	1651(5)	1945(5)	H(102)	709(6)	146(5)	203(5)
C(9)	13396(8)	560(7)	3159(7)	H(103)	693(6)	212(5)	363(5)
C(10)	7290(8)	1262(6)	3002(6)	H(111)	970(6)	304(5)	512(5)
C(11)	9644(8)	3187(6)	4204(5)	H(112)	903(6)	360(5)	383(5)
C(12)	11232(9)	1688(6)	685(6)	H(113)	1046(5)	392(5)	426(5)
				H(121)	1085(6)	234(5)	34(5)
				H(122)	1216(9)	123(8)	71(8)
				H(123)	1046(7)	106(6)	14(7)
				HO(13)	1380(7)	229(6)	520(6)

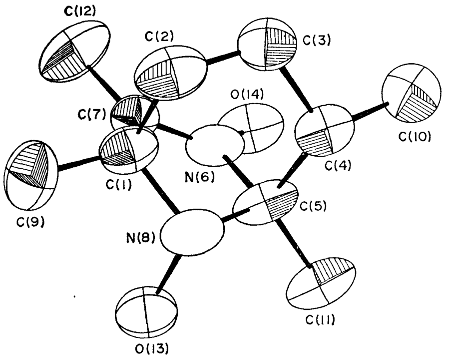


Fig. 1. A perspective drawing of **1** and the numbering scheme.

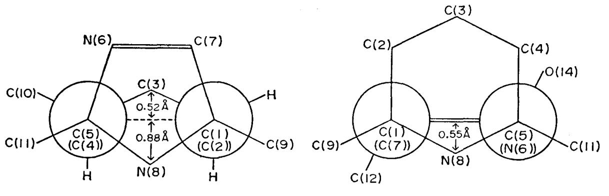


Fig. 2. Schematic drawings of the chair and half-chair forms.

membered, six-membered, and five-membered rings have a boat, chair, and half-chair comformations, respectively. All the methyl groups on the six-membered ring are equatorial, and the five-membered ring is joined to the six-membered ring through two axial-type bonds. The six- and five-membered rings are at an angle of 72.58°, *i.e.*, almost perpendicular to each other. C(1), C(2), C(4), and C(5) atoms in the six-membered ring, and C(1), N(6), C(5), and C(7) atoms in the five-membered ring are almost on a plane, respectively. The schematic drawings of the chair and half-chair forms are given in Fig. 2, using Newman's projection formula.

TABLE 3. BOND DISTANCES

Bond	Distances (l/Å)	Bond	Distances (l/Å)
N(8)-O(13)	1.455(6)	N(6)-O(14)	1.293(6)
N(8)-C(1)	1.492(7)	N(8)-C(5)	1.454(8)
N(6)-C(5)	1.524(6)	N(6)-C(7)	1.323(7)
C(1)-C(2)	1.542(8)	C(1)-C(7)	1.481(8)
C(1)-C(9)	1.537(10)	C(2)-C(3)	1.534(11)
C(3)-C(4)	1.528(8)	C(4)-C(5)	1.522(8)
C(4)-C(10)	1.547(10)	C(5)-C(11)	1.516(8)
C(7)-C(12)	1.483(9)		

TABLE 4. BOND ANGLES

Bond	Angle (ϕ/°)	Bond	Angle (ϕ/°)
O(13)-N(8)-C(1)	107.7(4)	O(13)-N(8)-C(5)	107.4(4)
C(1)-N(8)-C(5)	101.2(4)	O(14)-N(6)-C(5)	122.3(4)
O(14)-N(6)-C(7)	129.0(5)	C(5)-N(6)-C(7)	108.7(4)
N(8)-C(1)-C(2)	105.3(5)	N(8)-C(1)-C(7)	104.2(5)
N(8)-C(1)-C(9)	111.7(5)	C(2)-C(1)-C(7)	109.4(5)
C(2)-C(1)-C(9)	111.2(5)	C(7)-C(1)-C(9)	114.5(5)
C(1)-C(2)-C(3)	111.0(5)	C(2)-C(3)-C(4)	113.0(5)
C(3)-C(4)-C(5)	111.2(5)	C(3)-C(4)-C(10)	109.2(5)
C(5)-C(4)-C(10)	114.6(5)	N(8)-C(5)-N(6)	103.5(4)
N(8)-C(5)-C(4)	106.6(4)	N(8)-C(5)-C(11)	114.9(5)
N(6)-C(5)-C(4)	106.8(4)	N(6)-C(5)-C(11)	111.2(5)
C(4)-C(5)-C(11)	113.1(5)	N(6)-C(7)-C(1)	108.3(5)
N(6)-C(7)-C(12)	120.7(5)	C(1)-C(7)-C(12)	130.5(5)

Figure 3 shows the crystal structure viewed along the b-axis. Only oxygen atoms take part in the hydrogen bond; O(13) forms a intermolecular hydrogen bond with O(14), the O(13)···O(14) distance being 2.659(5) Å.

Figure 4 shows the mass spectrum of **1**, which is

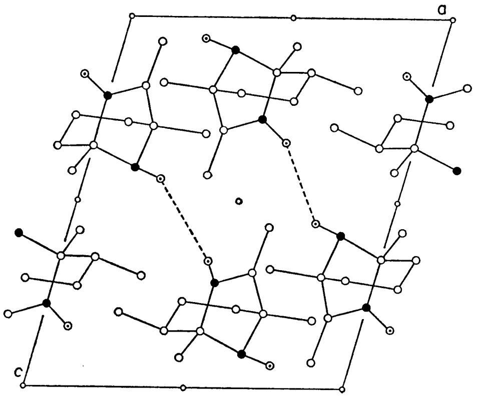
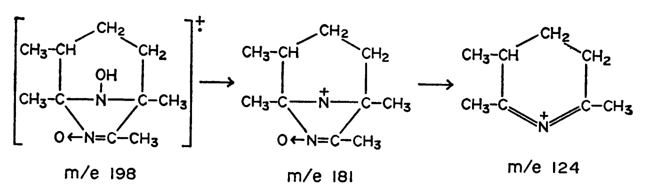


Fig. 3. The projection of the crystal structure along the b-axis.
○: Carbon, ●: nitrogen, ⊙: oxygen.

characterized by the appearance of peaks *m/e* 198 (M^+), 181, and 124, and can be satisfactorily explained on the basis of the following fragmentation pattern.[5]



As can be expected from the structure, ^{13}C-NMR spectrum of **1**, shown in Fig. 5, shows four quartet (δ=9.24, 14.06, 16.02, and 18.94), two triplet (δ=27.73 and 32.70), one doublet (δ=36.51), and three singlet peaks (δ=71.88, 98.97, and 142.88). The quartet, triplet, and doublet peaks correspond to the methyl, methylene, and methyne carbons, respectively, and it can be presumed that the singlet peaks at 71.88, 98.97, and 142.88 ppm are assigned to the tertiary carbons linked by $\mathrm{N{-}C}\langle$, $^{\mathrm{N}}_{\mathrm{N}}\!\rangle\mathrm{C}\langle$, and $^{\ominus}_{\mathrm{O}}\!\rangle\overset{\oplus}{\mathrm{N}}{=}\mathrm{C}\langle$ bonds, respectively.

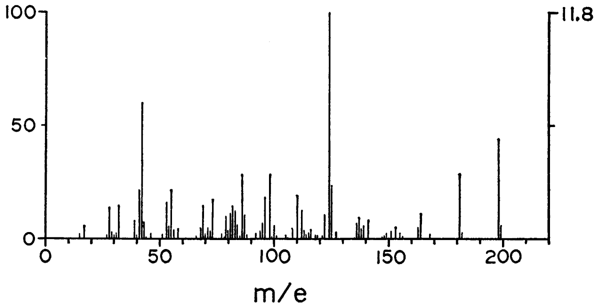


Fig. 4. Mass spectrum of **1**.

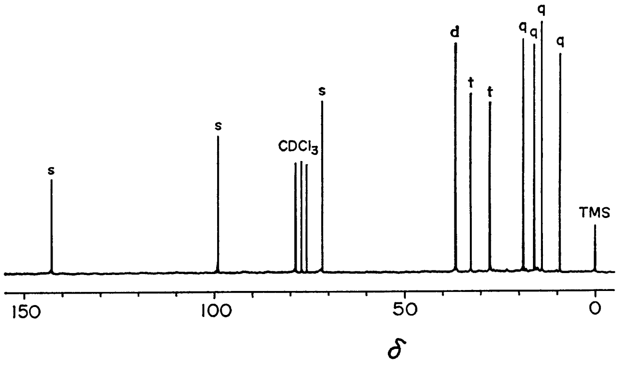


Fig. 5. ^{13}C-NMR spectrum of **1**.

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