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Dioxopyrrolines. XLI.[1] X-Ray Crystallographic Determination of the Stereochemistry of an Azatricyclo[5.3.0.0^{2,6}]decane Derivative Obtained by Photocycloaddition of Cyclopentadiene to 4-Ethoxycarbonyl-5-phenyl-1*H*-pyrrole-2,3-dione

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The stereochemistry of one of the photoadduct of cyclopentadiene to 4-ethoxycarbonyl-5-phenyl-1*H*-pyrrole-2,3-dione, 6-ethoxycarbonyl-2-phenyl-3-azatricyclo[5.3.0.0^{2,6}]decan-9-ene-4,5-dione, was establised as *cis–syn–cis* by an X-ray crystallographic analysis.

Keywords——dioxopyrroline; 1*H*-pyrrole-2,3-dione; cyclopentadiene; photocycloaddition; cyclobutane; X-ray analysis; stereochemistry

Previously, we reported that the photocycloaddition reaction of 4-ethoxycarbonyl-5-phenyl-1*H*-pyrrole-2,3-dione (**1**) to cyclopentadiene afforded three photoadducts, a dihydropyridone (**2**), a methanohydroindole (**3**) and a cyclobutane (**4**).[2] The structures of the major adducts (**2a** and **3a**) were unequivocally established by X-ray crystallographic analyses of the bromoderivatives (**2b** and **3b**).[2] However, the structure of **4a** was elucidated only from the spectral data, since neither **4a** nor **4b** gave appropriate single crystals for X-ray analysis at that time.

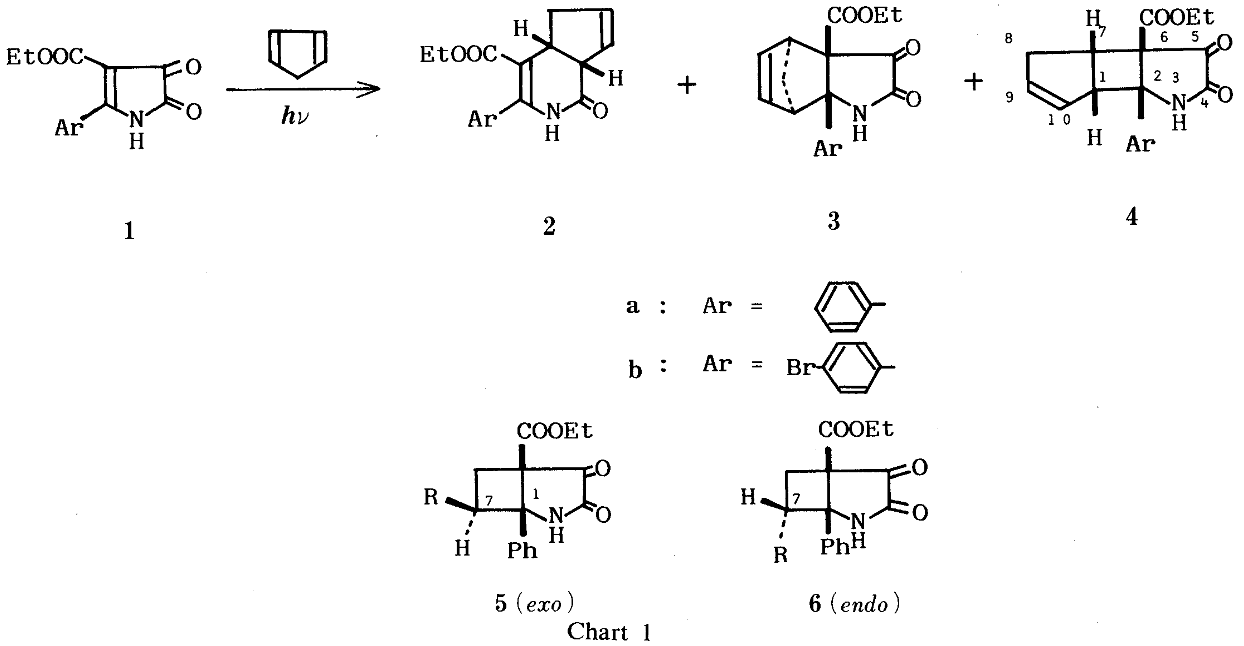

Chart 1

TABLE I. The Chemical Shifts of C-7 Proton and C-7 Carbon in the ^{1}H-NMR and ^{13}C-NMR Spectra of the *exo* (**5**) and *endo* Isomers (**6**)

R	*exo* (**5**)		*endo* (**6**)	
	$\delta_{\text{H-7}}$	$\delta_{\text{C-7}}$	$\delta_{\text{H-7}}$	$\delta_{\text{C-7}}$
Vinyl	3.32	52.1	4.13	41.6
(*E*)-Propenyl	3.30	52.0	4.04	41.9
(*Z*)-Propenyl	3.50	47.5	4.33	37.3
Cyclobutane (**4a**)			4.04	56.7

^{1}H- and ^{13}C-NMR: proton and carbon-13 nuclear magnetic resonance.

Our original assignment is based on the fact that the *exo* and *endo* isomers, **5** and **6**, can be differentiated from the C-7 proton chemical shift: *i.e.*, the C-7 proton signals of the *exo* isomers (**5**) always appear at higher magnetic field than those of the corresponding *endo* isomers (**6**)[3] (see Table I). The observed chemical shift of the C-1 proton (which corresponds to the C-7 proton in **5** or **6**) in **4a** (δ 4.04) falls in the range of *endo* isomers than that of *exo* isomers. From this fact, together with evidence that the ring juncture is *cis* ($J_{\text{H}_1-\text{H}_7}=7$ Hz), the stereochemistry of **4** was considered to be *cis–syn–cis*.

However, the following conflicting evidence found later[3] made the above assignment uncertain: *i.e.*, the C-7 carbon chemical shifts of the *endo* isomers (**6**) are more shielded by *ca.* 10 ppm than those of the *exo* isomers (**5**) (see Table I). The observed C-1 chemical shift (δ 56.7) of **4a** was far more deshielded than that expected for an *endo* isomer, rather suggesting that the substituent at the position is occupying an *exo* orientation. Although the carbon chemical shift is known to be very sensitive to the nature of the relevant carbon (ring size, *etc.*), this unusual deshielded C-1 signal suggested the revised configuration, *cis–anti–cis*.[4]

In order to resolve the above inconsistency we tried to determine the molecular structure of **4** by X-ray analysis and have now succeeded in preparing suitable single crystals from **4a** by repeated crystallization from a mixed solvent of ether, dichloromethane and methanol.

Experimental

Photocycloaddition of Cyclopentadiene to Dioxopyrroline (1a)——**1a** (4.0 g) and cyclopentadiene (6.7 g) in dimethoxyethane (350 ml) were irradiated for 50 min under stirring at -50 °C using a 300 W high-pressure mercury lamp with a Pyrex filter. After evaporation of the solvent, the residue in benzene was chromatographed over SiO_2. Elution with benzene gave the dihydropyridone (**2a**) (1.06 g, 24%), colorless needles from CH_2Cl_2–Et_2O, mp 108–110 °C. Elution of benzene–CH_2Cl_2 (1 : 1) gave a mixture of **3a** and **4a**, which were separated by fractional crystallization from CH_2Cl_2–Et_2O and by a preparative medium-pressure liquid chromatography using AcOEt–*n*-hexane (1 : 1) as an eluant, giving the hydroindole (**3a**) (820 mg, 16.5%), colorless prisms from CH_2Cl_2–Et_2O, mp 167—168 °C and the cyclobutane (**4a**) (490 mg, 10%), colorless prisms, mp 202—203 °C. The adducts (**2a**, **3a**, and **4a**) were shown to be identical with the compounds reported previously by spectral comparisons.[2] Single crystals of **4a** were grown from a solvent of ether–CH_2Cl_2–methanol as colorless prisms, mp 203—204 °C.

Crystallographic Measurement——The crystal data were collected on a Rigaku Denki computer-controlled four-circle diffractometer using Cu-K_α radiation. The intensities of all the reflections with 2θ values up to 150 ° of (hkl) and ($\bar{h}kl$) were measured by the ω–2θ scanning technique at a scan rate of 8 ° per min. The backgrounds were measured at both ends of the scan range for 5.0 s. Three standard reflections were measured every 50 min, and showed no significant variation with time. The intensity data were corrected for the background count and for the usual Lorentz and polarization effects. In total, 2388 independent non-zero reflections were measured.

Crystal Data: $C_{18}H_{17}NO_4$. $M=311.32$. Monoclinic. $a=16.485$ (6), $b=12.845$ (5), $c=7.680$ (3) Å. $\beta=107.22$ ° (3). $V=1553.3$ Å^3, $D_c=1.331$ g/cm^3, $z=4$. Space group: $P2_1/a$. Crystal size: $0.4\times0.4\times0.4$ mm.

Structure Analysis and Refinement——The structure was solved by the direct method using MULTAN[5] and refined by the block-diagonal least-squares procedure with anisotropic factors, using 2388 reflections. Inclusion of H atoms with isotropic temperature factors gave a final R value of 6.44%. The atomic parameters, an ORTEP drawing

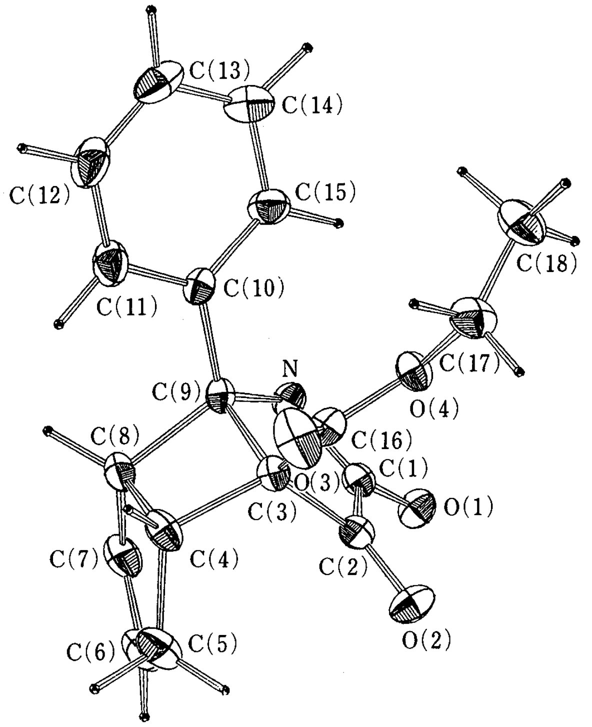

Fig. 1. ORTEP Drawing of **4a** and the Atomic Numbering

TABLE II. Positional Parameters (× 10^4) with Their Estimated Standard Deviations (in Parentheses) and Equivalent Isotropic Thermal Parameters ($Å^2$) of the Cyclobutane (**4a**)

Atom	x	y	z	B_{eq}/B_{iso}
O1	13 (2)	3811 (2)	1263 (3)	3.0
O2	711 (2)	1746 (2)	1089 (4)	3.6
O3	2296 (2)	1469 (3)	−1672 (5)	5.1
O4	2377 (1)	2800 (2)	268 (4)	3.0
N	448 (2)	4077 (2)	−1301 (4)	2.5
C1	331 (2)	3524 (3)	80 (5)	2.4
C2	693 (2)	2418 (3)	4 (5)	2.5
C3	1031 (2)	2385 (3)	−1645 (5)	2.4
C4	459 (2)	1792 (3)	−3344 (6)	3.3
C5	−223 (3)	1061 (3)	−3046 (7)	4.4
C6	−935 (3)	1794 (4)	−3107 (6)	4.3
C7	−807 (2)	2747 (3)	−3635 (6)	3.7
C8	16 (2)	2847 (3)	−4070 (5)	3.0
C9	738 (2)	3470 (3)	−2614 (5)	2.4
C10	1360 (2)	4053 (3)	−3337 (5)	2.6
C11	1481 (3)	3780 (4)	−4998 (6)	4.1
C12	2042 (3)	4327 (4)	−5677 (6)	4.8
C13	2504 (3)	5135 (4)	−4721 (7)	4.4
C14	2411 (3)	5398 (3)	−3046 (7)	4.2
C15	1837 (3)	4865 (3)	−2363 (6)	3.5
C16	1967 (2)	2144 (3)	−1059 (5)	2.9
C17	3304 (2)	2693 (4)	958 (7)	4.2
C18	3675 (3)	3730 (4)	1577 (7)	4.8

$$B_{eq}=\frac{4}{3}\sum_i\sum_j\beta_{ij}\boldsymbol{a}_i\boldsymbol{a}_j .$$

TABLE III. Bond Lengths (Å) of **4a** with Their Estimated Standard Deviations (in Parentheses)

Atoms	Distance (Å)	Atoms	Distance (Å)	Atoms	Distance (Å)
O1–C1	1.232 (4)	C3–C4	1.563 (4)	C9–C10	1.502 (5)
O2–C2	1.194 (4)	C3–C9	1.586 (4)	C10–C11	1.393 (6)
O3–C16	1.191 (5)	C3–C16	1.507 (4)	C10–C15	1.385 (5)
O4–C16	1.341 (4)	C4–C5	1.533 (6)	C11–C12	1.380 (7)
O4–C17	1.467 (4)	C4–C8	1.562 (5)	C12–C13	1.365 (6)
N–C1	1.336 (4)	C5–C6	1.495 (6)	C13–C14	1.382 (7)
N–C9	1.463 (4)	C6–C7	1.326 (6)	C14–C15	1.390 (6)
C1–C2	1.549 (4)	C7–C8	1.496 (6)	C17–C18	1.484 (6)
C2–C3	1.528 (5)	C8–C9	1.589 (4)		

of the molecule, bond lengths, and bond angles are given in Fig. 1 and Tables II—IV, respectively.

Results and Discussion

The result of X-ray analysis unequivocally established the stereochemistry of the photoadduct (**4a**) as *cis–syn–cis*, in agreement with our original assignment.[2)] The results also showed that the cyclobutane ring is distorted, with elongation of C_2–C_6 (1.59 Å) and C_1–C_2 (1.59 Å) as compared to the other bonds in the cyclobutane ring (1.56 Å).

Table IV. Bond Angles of **4a** with Their Estimated Standard Deviations (in Parentheses)

Atoms	Angle (°)	Atoms	Angle (°)
C16–O4–C17	116.9 (3)	C4–C8–C9	90.7 (2)
C1–N–C9	114.6 (2)	C7–C8–C9	115.2 (3)
O1–C1–N	128.2 (3)	N–C9–C3	105.2 (2)
O1–C1–C2	123.7 (3)	N–C9–C8	115.1 (3)
N–C1–C2	108.1 (3)	N–C9–C10	112.8 (2)
O2–C2–C1	124.6 (3)	C3–C9–C8	87.0 (2)
O2–C2–C3	128.2 (3)	C3–C9–C10	117.7 (2)
C1–C2–C3	107.2 (2)	C8–C9–C10	116.3 (3)
C2–C3–C4	115.3 (3)	C9–C10–C11	120.8 (3)
C2–C3–C9	103.3 (2)	C9–C10–C15	121.1 (3)
C2–C3–C16	110.5 (2)	C11–C10–C15	118.1 (3)
C4–C3–C9	90.7 (2)	C10–C11–C12	120.8 (4)
C4–C3–C16	117.4 (3)	C11–C12–C13	120.9 (4)
C9–C3–C16	117.6 (3)	C12–C13–C14	119.2 (4)
C3–C4–C5	117.5 (3)	C13–C14–C15	120.4 (3)
C3–C4–C8	88.8 (2)	C10–C15–C14	120.6 (4)
C5–C4–C8	107.4 (3)	O3–C16–O4	124.9 (3)
C4–C5–C6	102.3 (3)	O3–C16–C3	125.3 (3)
C5–C6–C7	113.4 (4)	O4–C16–C3	109.8 (3)
C6–C7–C8	112.5 (3)	O4–C17–C18	108.5 (3)
C4–C8–C7	101.9 (3)		

The photocycloaddition of cyclopentenone–cyclopentene pairs is known usually to form the cyclobutane having *cis–anti–cis* stereochemistry as shown in many examples.[6] This is, we believe, the first example demonstrating with unequivocal structural proof that the photocycloaddition of a cyclopentenone–cyclopentene pair yields the cyclobutane having a 5-4-5 ring system with *cis–syn–cis* stereochemistry.

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