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Dioxopyrrolines. XXXII.[1] X-Ray Determination of the Molecular Structure of a Photoadduct of 2-Trimethylsilyloxybutadiene to 3-Ethoxycarbonyl-2-phenyl-Δ^2-pyrroline-4,5-dione

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The stereochemistry of the photocycloadduct of 2-trimethylsilyloxybutadiene to 3-ethoxycarbonyl-2-phenyl-Δ^2-pyrroline-4,5-dione (**1**) was established as 5-ethoxycarbonyl-1-phenyl-7-*endo*-trimethylsilyloxy-7-*exo*-vinyl-2-azabicyclo[3.2.0]heptane-3,4-dione (**2**) by X-ray analysis.

Keywords——Δ^2-pyrroline-4,5-dione; 2-trimethylsilyloxybutadiene; photocycloaddition; 2-azabicyclo[3.2.0]heptane-3,4-dione; X-ray analysis; stereochemistry

Photocycloaddition of a substituted olefin to 3-ethoxycarbonyl-2-phenyl-Δ^2-pyrroline-4,5-dione (**1**) proceeds in regio- and stereo-selective manner to give a single 2+2 adduct, 5-ethoxycarbonyl-1-phenyl-7-substituted-2-azabicyclo[3.2.0]heptane-3,4-dione.[2] Interestingly, the stereochemistry of the product varies depending on the nature of the substituent on the olefin; olefins carrying a moderately polar substituent such as a vinyl or phenyl group (polar olefins) give the *exo*-adduct (**3**), while olefins carrying a very polar O-substituent (very polar olefins) such as ethyl vinyl ether or vinyl acetate give the *endo*-adduct (**4**) as a major product.[2b] 2-Trimethylsilyloxybutadiene also undergoes smooth cycloaddition to **1** in a highly site-, regio-, and stereo-selective manner to give a 7-trimethylsilyloxy-7-vinyl cyclobutane (**2**) as a single product, whose structure except for the stereochemistry has already been established.[3] The stereochemistry was tentatively assigned as *exo*-vinyl and *endo*-trimethylsilyloxy (OTMS).

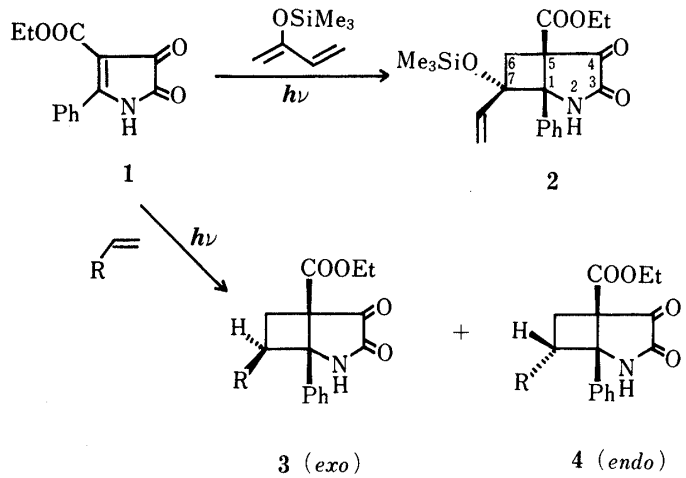

Chart 1

However, there are several chemical findings regarding the stereochemistry of **2** which appear to be conflicting. Thermolysis of **2** gave a hydroindole (**6**) exclusively,[3] which is the product expected from the *exo*-vinyl isomer, since it had already been shown that on pyrrolysis of 7-hydrogen-7-vinyl derivatives the *exo* isomer (**8**) yields the hydroindole (**9**), while the *endo* isomer (**10**) gives a Cope rearrangement product (**11**).[4] On the other hand, acidic treatment of **2** produced **7**, which arises from intramolecular Prins-type cyclization between the vinyl group and C_4 carbonyl with concomitant skeletal 1,2-rearrangement, thus suggesting the *endo*-vinyl configuration of the intermediary hydroxy compound, as shown in the structure **5**.[5] Thus, we carried out an X-ray analysis to determine the stereochemistry unambiguously. A suitable single crystal of the 7-OTMS-7-vinyl derivative was obtained, and used for the analysis.

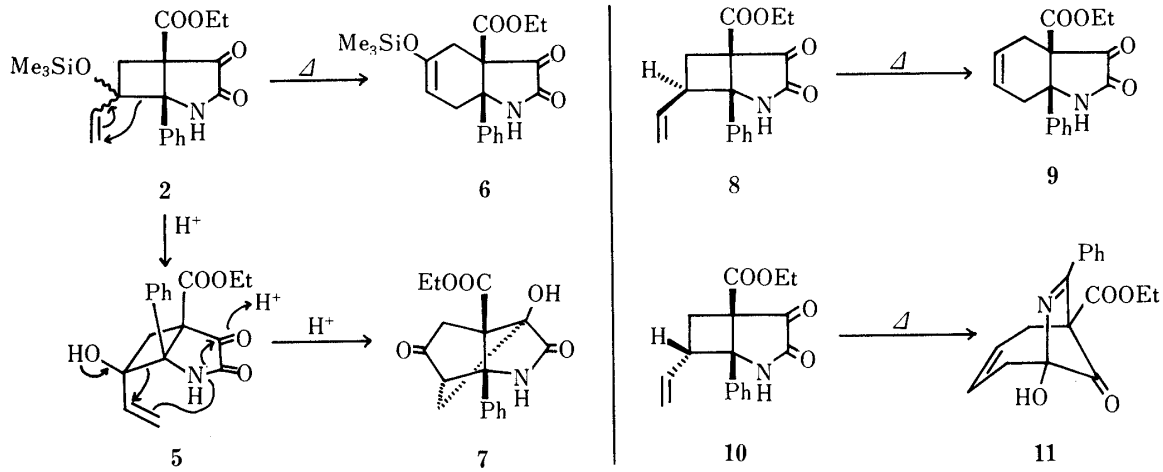

Chart 2

Experimental

Photocycloaddition of 2-Trimethylsilyloxybutadiene to the Dioxopyrroline (1)——The dioxopyrroline (**1**) (2.0 g) and 2-trimethylsilyloxybutadiene (2.3 g, 2 eq) in dimethoxyethane (300 ml) were irradiated for 1 h under stirring at 0 °C using a 300 W high pressure mercury lamp with a Pyrex filter. After evaporation of the solvent, the residue was dissolved in CH_2Cl_2 and passed through a short column of Florisil. Concentration of the eluate gave **2** (2.2 g; 70%), which crystallized on trituration with Et_2O. Single crystals were grown from Et_2O–acetone as colorless prisms, mp 176—178 °C. IR (Nujol) cm^{-1}: 3190, 3100 (NH), 1780, 1760, and 1730 (C=O). ^{1}H-NMR (100 MHz in $CDCl_3$) δ:

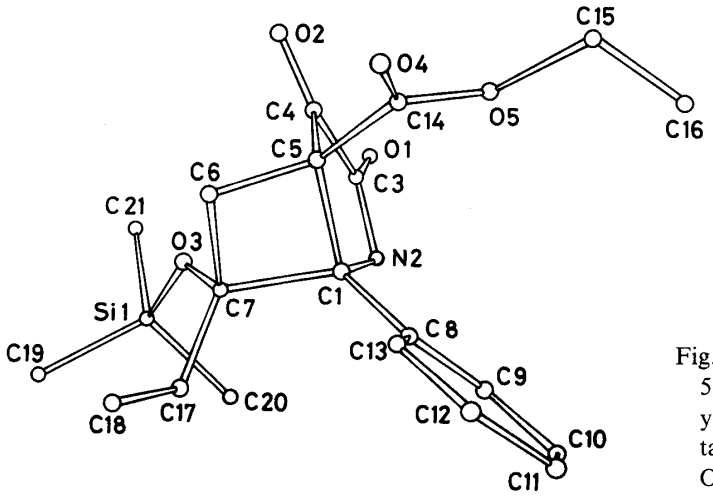

Fig. 1. An ORTEP Drawing of the Molecule of 5-Ethoxycarbonyl-1-phenyl-7-*endo*-trimethylsilyloxy-7-*exo*-vinyl-2-azabicyclo[3.2.0]heptane-3,4-dione (**2**) with Hydrogen Atoms Omitted

TABLE I. Positional Parameters ($\times 10^4$) with Their Estimated Standard Deviations (in Parentheses) and Equivalent Isotropic Thermal Parameters (Å^2) of 5-Ethoxycarbonyl-1-phenyl-7-*endo*-trimethylsilyloxy-7-*exo*-vinyl-2-azabicyclo[3.2.0]heptane-3,4-dione (**2**)

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

	X	*Y*	*Z*	B_{eq}
N 2	4857 (4)	6198 (4)	1243 (4)	4.62
O 1	3720 (4)	6191 (4)	−1060 (4)	6.04
O 2	2467 (4)	8607 (4)	−469 (4)	6.54
O 3	2453 (3)	5453 (4)	619 (3)	5.36
O 4	4991 (5)	10983 (4)	3499 (5)	8.17
O 5	5878 (4)	10028 (4)	2522 (4)	6.59
Si 1	1819 (2)	3596 (2)	−295 (2)	5.62
C 1	4840 (4)	6919 (5)	2359 (5)	4.36
C 3	3986 (5)	6687 (5)	68 (5)	4.81
C 4	3379 (5)	8019 (5)	380 (5)	4.80
C 5	4110 (5)	8384 (5)	1949 (5)	4.72
C 6	3166 (5)	7962 (5)	2218 (6)	5.38
C 7	3487 (5)	6267 (5)	2089 (5)	4.87
C 8	6242 (5)	7144 (5)	3834 (5)	4.66
C 9	7307 (5)	6460 (7)	4028 (6)	6.26
C 10	8619 (6)	6704 (8)	5394 (7)	7.77
C 11	8859 (6)	7648 (8)	6587 (6)	7.43
C 12	7761 (6)	8308 (7)	6368 (6)	7.02
C 13	6461 (5)	8057 (6)	5018 (5)	5.92
C 14	5034 (5)	9970 (5)	2765 (5)	5.54
C 15	6941 (7)	11460 (8)	3321 (9)	9.29
C 16	8209 (8)	11002 (12)	3858 (11)	12.93
C 17	3688 (5)	5364 (6)	3028 (5)	5.94
C 18	3306 (7)	5786 (8)	3798 (6)	7.77
C 19	813 (8)	2719 (9)	51 (9)	9.52
C 20	3216 (8)	2470 (7)	100 (10)	9.61
C 21	661 (9)	3718 (9)	2167 (7)	10.57

TABLE II. Bond Lengths of **2** with Their Estimated Standard Deviations (in Parentheses)

Bond	Length Å	Bond	Length Å
C_1–N_2	1.452 (19)	C_8–C_{13}	1.401 (26)
C_1–C_5	1.572 (26)	C_9–C_{10}	1.402 (50)
C_1–C_7	1.632 (21)	C_{10}–C_{11}	1.398 (28)
C_1–C_8	1.510 (53)	C_{11}–C_{12}	1.395 (21)
N_2–C_3	1.343 (34)	C_{12}–C_{13}	1.386 (50)
C_3–C_4	1.526 (21)	C_{14}–O_4	1.181 (21)
C_3–O_1	1.223 (19)	C_{14}–O_5	1.317 (12)
C_4–C_5	1.523 (32)	C_{15}–C_{16}	1.389 (27)
C_4–O_2	1.184 (32)	C_{15}–O_5	1.490 (46)
C_5–C_6	1.542 (16)	C_{17}–C_{18}	1.352 (18)
C_5–C_{14}	1.517 (44)	Si_1–C_{19}	1.859 (22)
C_6–C_7	1.558 (14)	Si_1–C_{20}	1.855 (31)
C_7–C_{17}	1.486 (21)	Si_1–C_{21}	1.865 (22)
C_7–O_3	1.423 (52)	Si_1–O_3	1.653 (40)
C_8–C_9	1.375 (20)		

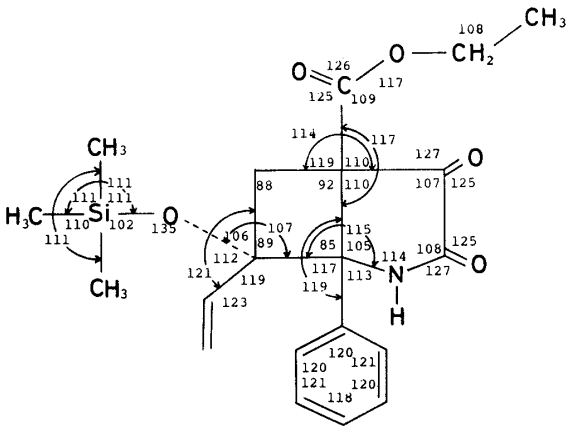

Fig. 2. Bond Angles (°) with Maximum Standard Deviation 2°

0.08 (9H, s, $\underline{Me_3}Si$–), 0.77 (3H, t, $J=7$ Hz, –O–CH_2–$\underline{CH_3}$), 2.37 and 3.53 (each 1H, d, $J=14$ Hz, C_6-methylene), 3.88 (2H, q, $J=7$ Hz, –O$\underline{CH_2}CH_3$), 5.05—5.57 (3H, m, vinyl H), 7.32 (5H, s, PhH). High resolution MS, Calcd for $C_{20}H_{25}NO_5Si$: m/z ($\overline{M^+}$) 387.1502. Found: m/z 387.1538.

Crystallographic Measurement——A computer-controlled Rigaku Denki AFC-5 four-circle auto-diffractometer was used for all measurements. The intensities of all the reflections in the range of $3° < 2\theta < 55°$ were measured using the $\omega - 2\theta$ scan method with a scan speed of 2°/min in 2θ. Of the total of 5194 independent reflections obtained by the use of monochromated Mo-$K\alpha$ radiation, 3729 reflections had intensities above the $3\sigma(\pm)$ level, and they were used in the calculation. No absorption correction was made.

Crystal Data——$C_{20}H_{25}NO_5Si$. $M=387.5$. Triclinic. $a=12.870$ (4), $b=8.926$ (2), $c=12.909$ (5) Å, $\alpha=103.18$ (3)°, $\beta=130.77$ (2)°, $\gamma=88.45$ (3)°, $U=1078.5$ Å^3, $D_c=1.19$ g/cm^3, $Z=2$, μ(Mo-$K\alpha$)$=0.6$ cm^{-1}. Space group $P\bar{1}$. Crystal size, $0.50 \times 0.50 \times 0.30$ mm^3.

Structure Analysis and Refinement——The structure was solved by the direct method using MULTAN and refined by the block-diagonal least-squares procedure with the assumption of positional anisotropic thermal parameters for all non-hydrogen atoms. The final R-value was 0.079. The atomic parameters, an ORTEP drawing of the molecule, bond lengths, and bond angles are given in Tables I and II, and Figs. 1 and 2, respectively.

Results and Discussion

The result of X-ray analysis rigidly established the stereochemistry of the adduct (**2**) as 7-*exo*-vinyl and 7-*endo*-OTMS, in agreement with our expectation. The results also showed that the cyclobutane ring is abnormally distorted, elongating the C_1–C_7 bond (1.632 Å) as compared to the other bonds of the cyclobutane ring. This suggests high reactivity of this bond as exemplified in the thermal[4] or tetra-*n*-butylammonium fluoride (TBAF)-induced [1,3]shift[6] of the compound to a hydroindole.

The rearrangement of the compound (**2**) to a 2-azatricyclo[4.3.0.0^{4,9}]nonane-3,7-dione (**7**)[5] therefore must involve an epimerization at C-7 under acidic conditions, probably at the stage of the alcohol (**5**). An intramolecular Prins reaction is otherwise impossible. Although an analogous epimerization under basic conditions was reported previously,[7] details of this rearrangement will be fully discussed in a future communication.

References and Notes

1) Part XXXI: See ref. 5. This paper also constitutes Part 8 of our series on 2-azabicyclo[3.2.0]heptane-3,4-diones.
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