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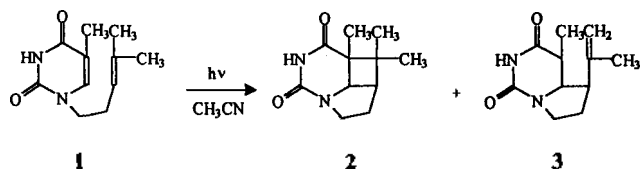
Synthesis and Crystal Structure of 1,3-Diaza-5,6,6-trimethyltricyclo[5,2,1,0^{5,10}]decan-2,4-dione

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Intramolecular [2+2] photocycloaddition reaction of olefinic cycloenones are well-established synthetic methods of complex carbocyclic and heterocyclic compounds, since this simple reaction provides good regio- and stereospecificity in relatively high yield. The retro-ene reactions or chemical cleavages of cyclobutane ring of the photoadduct transform annelative two carbon ring or carbon hetero ring expansion of original cycloenones, otherwise those are difficult to obtain by ordinary synthetic methods.¹ Direct and/or pyrex filtered irradiation of N¹-(4-methyl-3-pentenyl) thymine (1) with a 12 W low pressure Hg lamp in CD₃CN at room temperature for 10 hr gave (2) and (3) in ratio 4.9 : 3.5.²



Experimental

1,3-Diaza-5,6,6-trimethyltricyclo[5,2,1,0^{5,10}]decan-2,4-dione (2) and 1,3-Diaza-5-methyl-7(1-methylethenyl)bicyclo[4,3,0]nonan-2,4-dione (3). A solution of 1 in 250 mL of acetonitrile was irradiated with a 12 W low pressure Hg lamp for 15 hr under nitrogen stream. The solvent was removed and the residue was submitted to preparative TLC (silica gel) using methanol-methylenechloride (1 : 9) as the eluents. The isolated yield was 17 mg (33%) of 2 and 21 mg (41%) of 3. Compound 2, mp 204-206 °C; ¹H NMR (200 MHz, CDCl₃) δ 0.90 (s, 3H), 1.05 (s, 3H), 1.34 (s, 3H), 1.82-1.93 (m, 2H), 2.61 (td, *J*=6.1, 5.6 Hz, 1H), 3.16 (ddd, *J*=1.2, 2.2, 8.7, 8.7 Hz, 1H), 3.55 (d, *J*=6.2 Hz, 1H), 4.06-4.19 (m, 1H), 7.20 (s, 1H); IR (KBr), 1703 cm⁻¹ (ν_{C=O}); EIMS *m/z* 208 (M⁺). Compound 3, mp 220-222 °C; ¹H NMR (200 MHz, CDCl₃) δ 1.10 (d, *J*=6.7 Hz, 3H), 1.67 (s, 3H), 1.90-2.18 (m, 2H), 2.32-2.42 (m, 1H), 2.89 (dd, *J*=6.3, 6.2 Hz, 1H), 3.45 (dd, *J*=12.7, 5.8 Hz, 1H), 3.54-3.62 (m, 2H), 4.70 (s, 1H), 4.86 (d, *J*=1.3 Hz, 1H), 7.17 (s, 1H); IR (KBr), 1721, 1691 cm⁻¹ (ν_{C=O}); EIMS *m/z* 208 (M⁺).

Crystallographic Studies. Small plate-like crystal was selected for X-ray analysis. Preliminary examination and data collection were performed with MoKα₁ radiation (λ=0.71073 Å) on an MXC3 diffractometer (Mac Science) equipped with an incident beam graphite monochromator. The unit cell parameters and the orientation matrix for data collection were obtained from the least-squares refinement using the setting angles of 15 reflections in the range 20° < 2θ(MoKα₁) < 28°. The monoclinic cell parameters and calculated volumes are a=13.113 (6) Å, b=7.174 (3) Å, c=11.836 (6) Å, β=99.99° (4). The systematic extinctions (0*k*0 : *k*=2*n*+1, *h*0*l* : *h*+*l*=2*n*+1) were indicative of the space group C_{2h}⁵-P2₁/c. Intensity data were collected with the ω-2θ scan techniques. The intensities of two standard reflections, measured every hundred reflections, showed no significant deviations during the data collection.

The initial positions for all non-hydrogen atoms were obtained by using direct methods of the SHELXS-86 program.⁴ The structure was refined by full matrix least-squares technique with the use of the SHELXL-93 program.⁵ Anisotropic thermal motion for non-hydrogen atoms and isotropic extinction parameters were included. The final cycle of refinement performed on Fo² with all 1715 unique reflections afforded residuals *w*R₂=0.1126 and the conventional R index based on the reflections having Fo > 4σ(Fo) is 0.0496. Additional crystallographic data and details of the data collection are given in Table 1. Final atomic positions for non-hydrogen and hydrogen atoms are listed in Table 2. Table 3 shows bond lengths and angles.

Results and Discussion

A view of the new compound is given in Figure 1. Table 4 presents least-squares planes of rings in the compound. The title compound is structurally similar to the tricyclic compound reported earlier.⁶ In this tricyclic system, the three rings (4,5,6-membered) are fused by the C5-C6, C7-C10, and N1-C10 bonds. The cyclobutane is a nearly ideal plane. The C6 atom in this ring deviates 0.401 Å from the least-squares plane defined by C5, C7, and C10 atoms. The thy-

Table 1. Crystal data and structure refinement for 1,3-Diaza-5,6,6-trimethyltricyclo[5.2.1.0^{5,10}]decan-2,4-dione

Formula weight	208.26
Space group	<i>C_{2h}⁵-P2₁/c</i>
a, Å	13.113(6)
b, Å	7.174(3)
c, Å	11.836(6)
β°, deg	99.99(4)
V, Å ³	1096.5(9)
Z	4
T, K	293(2)
Linear absorption coefficient, cm ⁻¹	0.88
Radiation	graphite monochromated MoKα ₁ (λ(Kα ₁) = 0.71073 Å)
Density (calc., g/cm ³)	1.261
Crystal size, mm ³	0.6 × 0.5 × 0.04
Scan type	ω-2θ
Scan speed, deg/min	5.0 in ω
Scan range, deg	1.0 + 0.35 tanθ
θ range for data collection, deg	1.58 to 23.99
Index ranges	-15 ≤ h ≤ 14, -8 ≤ k ≤ 0, 0 ≤ l ≤ 13
Reflections collected	1823
Independent reflections	1715 [R (int) = 0.0446]
R1 [F _o > 4σ(F _o)]	0.0496
wR2	0.1126
Goodness-of-fit on F ²	1.029

^aα and γ were constrained to be 90° in the refinement of cell parameters.

Table 2. Atomic coordinates (×10⁴) and equivalent isotropic displacement parameters (Å² × 10³) for 1,3-Diaza-5,6,6-trimethyltricyclo[5.2.1.0^{5,10}]decan-2,4-dione

atom	x	y	z	U(eq) or U [*]
N(1)	1028(2)	1088(3)	2627(2)	41(1)
N(3)	1334(2)	692(4)	4603(2)	46(1)
O(1)	-255(1)	122(3)	3545(2)	54(1)
O(2)	2914(2)	186(3)	5658(2)	65(1)
C(2)	648(2)	610(4)	3567(2)	41(1)
C(4)	2398(2)	559(4)	4731(2)	44(1)
C(5)	2853(2)	922(4)	3663(2)	44(1)
C(6)	3015(2)	841(4)	2897(2)	47(1)
C(7)	2467(2)	289(4)	1824(2)	51(1)
C(8)	1516(3)	-438(6)	1037(3)	58(1)
C(9)	584(3)	371(5)	1489(3)	51(1)
C(10)	2095(2)	1679(4)	2654(3)	46(1)
C(11)	2438(3)	-2577(5)	3180(3)	56(1)
C(12)	4134(3)	-1384(8)	2851(4)	77(1)
C(13)	3796(3)	2185(6)	3976(4)	69(1)
H(1)	1076(26)	496(51)	5190(30)	79(12)
H(2)	2971(23)	854(44)	1421(26)	68(9)
H(3)	1482(21)	-118(42)	199(27)	59(8)

H(4)	1460(23)	-1812(53)	1043(26)	70(10)
H(5)	281(23)	1435(47)	979(27)	69(10)
H(6)	11(25)	-496(48)	1529(28)	77(11)
H(7)	2108(22)	2901(46)	2496(25)	57(9)
H(8)	2468(24)	-3488(51)	2577(29)	76(11)
H(9)	1676(23)	-2315(39)	3144(22)	49(8)
H(10)	2799(24)	-2992(45)	3972(31)	74(10)
H(11)	4497(35)	-2052(64)	3672(42)	128(16)
H(12)	4544(29)	-349(56)	2716(30)	89(14)
H(13)	4132(26)	-2263(54)	2258(32)	84(12)
H(14)	4031(26)	2499(48)	3263(32)	79(11)
H(15)	4396(32)	1502(57)	4480(32)	95(13)
H(16)	3573(29)	3315(61)	4387(34)	100(14)

*U is for hydrogen atoms.

Table 3. Bond lengths [Å] and angles [deg] for 1,3-Diaza-5,6,6-trimethyltricyclo[5.2.1.0^{5,10}]decan-2,4-dione

N(1)-C(2)	1.339(3)	N(1)-C(10)	1.457(4)
N(1)-C(9)	1.465(4)	N(3)-C(2)	1.390(4)
N(3)-C(4)	1.381(4)	O(1)-C(2)	1.231(3)
O(2)-C(4)	1.215(3)	C(4)-C(5)	1.511(4)
C(5)-C(10)	1.516(4)	C(5)-C(13)	1.526(4)
C(5)-C(6)	1.592(4)	C(6)-C(11)	1.524(4)
C(6)-C(12)	1.528(4)	C(6)-C(7)	1.571(4)
C(7)-C(8)	1.514(5)	C(7)-C(10)	1.537(4)
C(2)-N(1)-C(10)	123.4(2)	C(2)-N(1)-C(9)	121.8(2)
C(10)-N(1)-C(9)	110.4(2)	C(2)-N(3)-C(4)	125.4(2)
O(1)-C(2)-N(1)	123.4(3)	O(1)-C(2)-N(3)	120.2(2)
N(1)-C(2)-N(3)	116.4(3)	O(2)-C(4)-N(3)	120.5(3)
O(2)-C(4)-C(5)	123.7(3)	N(3)-C(4)-C(5)	115.8(3)
C(4)-C(5)-C(10)	114.9(2)	C(4)-C(5)-C(13)	108.7(3)
C(10)-C(5)-C(13)	111.8(3)	C(4)-C(5)-C(6)	116.8(2)
C(10)-C(5)-C(6)	88.3(2)	C(13)-C(5)-C(6)	115.3(2)
C(11)-C(6)-C(12)	108.4(3)	C(11)-C(6)-C(7)	115.1(3)
C(12)-C(6)-C(7)	114.2(3)	C(11)-C(6)-C(5)	113.8(2)
C(12)-C(6)-C(5)	116.5(3)	C(7)-C(6)-C(5)	87.8(2)
C(8)-C(7)-C(10)	107.3(3)	C(8)-C(7)-C(6)	122.1(3)
C(10)-C(7)-C(6)	88.3(2)	C(7)-C(8)-C(9)	106.0(3)
N(1)-C(9)-C(8)	103.9(3)	N(1)-C(10)-C(5)	114.1(2)
N(1)-C(10)-C(7)	102.0(2)	C(5)-C(10)-C(7)	91.9(2)

mine is slightly distorted plane (max. dev. Å 0.099). The C10 atom which deviates 0.404 Å from the least-squares planes defined by N3, C2, N1, C4, and C5 atoms. The torsion angles of O2-C4-C5-C13 and C13-C5-C6-C11 are -44.0(4)° and 144.3(3)° respectively. As shown in the other related tricyclic compounds,⁷ the two molecules are bound with inversion symmetry paired together with the hydrogen bonding interactions between N3 and O1' (d(N3-O1') = 2.869 (3) Å, ∠(N3-H1...O1') = 171(3)°), where O1' relates O1 to an inversion center (Figure 2).

It is clear in the light of our analysis of structure of **2**, which has the feature that the carbonyl (C-4) and one of the proton at methyl group (at C-7) have very close site proximity and conformation, i.e., ∠O(2)-C(4)-H(8) = 132.8° and d(O(2)-H(8)) = 2.703 Å, and available to them to undergo

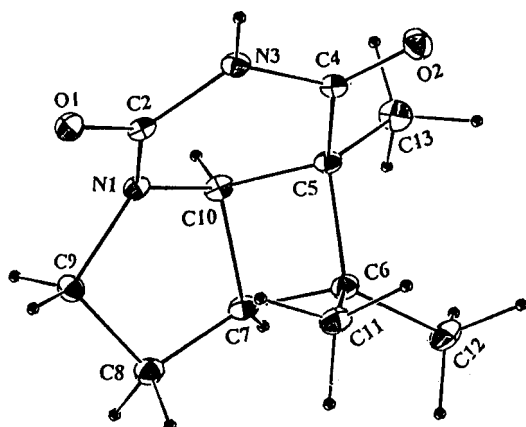


Figure 1.

Table 4. Least-squares planes for 1,3-Diaza-5,6,6-trimethyltricyclo[5.2.1.0^{5,10}]decan-2,4-dione

Cyclobutane		Thymine		Cyclopentane	
atom	distance(Å)	atom	distance(Å)	atom	distance(Å)
*C(5)	0	*N(1)	0.050(1)	*C(7)	-0.050(1)
*C(10)	0	*C(5)	-0.004(1)	*N(1)	0.052(1)
*C(7)	0	*C(2)	-0.099(2)	*C(9)	-0.078(2)
C(6)	-0.401(6)	*N(3)	0.098(2)	*C(8)	0.077(2)
		*C(4)	-0.044(2)	C(10)	-0.426(5)
		C(10)	0.404(4)		

*Indicates atom used to define planes

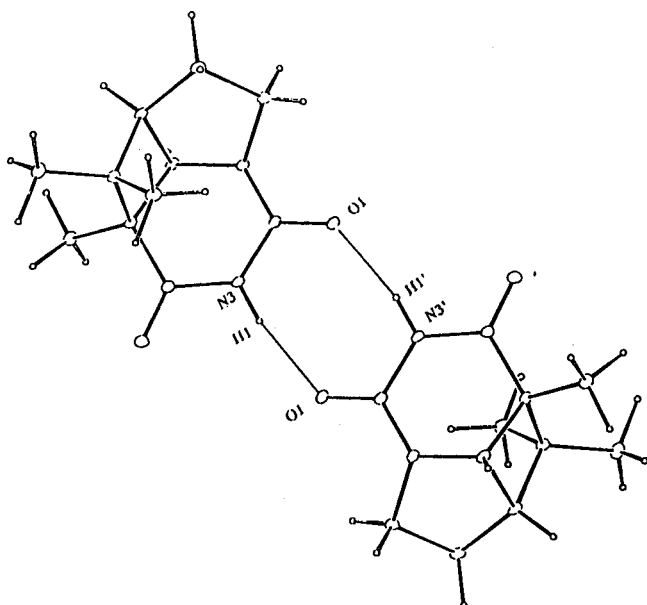
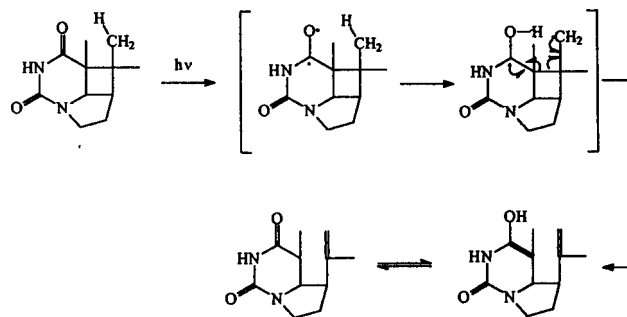
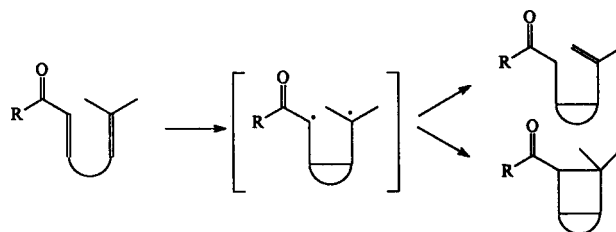


Figure 2.

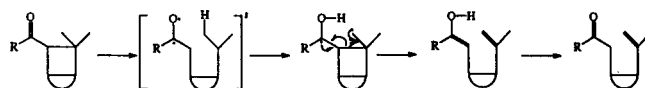
characteristic 1,5-hydrogen atom transfer by an intramolecular cyclic process with formation of a ketyl-like 1,4-biradical (Norrish type II).



That is to say, the methyl hydrogen (at C-7) in **2** can approach the ketone carbonyl (C-4) either from a perpendicular direction for direct interaction with the carbonyl 2π electrons or through an in-plane mode for initial interaction with the carbonyl nonbonding electrons. Thus, irradiation of **2** in CH_3CN with a 200W medium pressure Hg lamp or with a 12 W low pressure Hg lamp for 10 hr produced **3** in more than 89% yield. The structure and photochemistry of **2** can provide a valuable information relevant to mechanistic studies of enone-ene [2+2] photocycloaddition reactions which confront with some anomalies to explain the formation of fission products arising from cyclobutane ring as a side product, which has been generally explained by disproportionation process from initially formed 1,4-diradical intermediate.³



The structure of **2** demonstrates the formation of fission product of cyclobutane ring in enone-ene photoaddition reaction could derive in part as secondary n, π^* Type II photoprocess of carbonyl group of initial photoproduct depending on its structure.



Details of the results of photochemistry of **2** will be published in a forthcoming paper.

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Preparation and Characterization of $[\eta^5\text{-CpNi}\{\text{P}(\text{OMe})_2(=\text{O})\}_2]_3\text{Y}$

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Transition metal complexes containing $[\eta^5\text{-CpNi}\{\text{P}(\text{OMe})_2(=\text{O})\}_2]$ have been widely studied.^{1,2} But yttrium complexes of the ligand are not known. The coordination chemistry of yttrium has become considerable attraction since yttrium complexes reveal the catalytic activities for ring-opening polymerization³ or α -olefin polymerization.⁴ The common coordinate number of yttrium is seven or eight because of relatively large ionic radius⁵ and six coordinate complexes which are structurally well defined are very rare.^{6,7} We here report the crystal structure for a six-coordinate, homoleptic complex of yttrium.

Experimental

All manipulations were performed under an argon atmosphere using a double manifold vacuum system and Schlenk techniques at room temperature. Solvents were purified by standard methods and were freshly dried and distilled prior to use. YCl_3 was purchased from Aldrich Co. and used as received. $\text{H}_4\text{N}[\eta^5\text{-CpNi}\{\text{P}(\text{OMe})_2(=\text{O})\}_2]$ was prepared by the literature method.¹

¹H NMR spectrum was obtained in C_6D_6 and referenced to internal deuterated solvent and recalculated relative to TMS on a Bruker AM-300 spectrometer. Chemical analyses were carried out by the Chemical Analysis Laboratory at KBSC.

Preparation of $[\eta^5\text{-CpNi}\{\text{P}(\text{OMe})_2(=\text{O})\}_2]_3\text{Y}$. To a mixture of 1.5 mmol of $\text{H}_4\text{N}[\eta^5\text{-CpNi}\{\text{P}(\text{OMe})_2(=\text{O})\}_2]$ and 0.5 mmol of YCl_3 , 20 mL of dry THF was introduced. The resulting suspension was stirred at room temperature for 24 h and then the precipitate was filtered off. The filtrate

Table 1. Crystal data and structure refinement for $[\eta^5\text{-CpNi}\{\text{P}(\text{OMe})_2(=\text{O})\}_2]_3\text{Y}$

Empirical formula	$\text{C}_{27}\text{H}_{51}\text{Ni}_3\text{O}_{18}\text{P}_6\text{Y}$
Formula weight	1114.54
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/a$
Unit cell dimensions	$a = 18.428(2)$ Å $b = 11.535(2)$ Å $c = 21.793(2)$ Å $\beta = 107.213(9)^\circ$
Volume	4424.9(1) Å ³
Z	4
Density (calculated)	1.673 Mg/m ³
Absorption coefficient	2.838 mm ⁻¹
F(000)	2280
Absorpt.-correction T min	0.866
Absorpt.-correction T max	1.000
Crystal size	0.50 × 0.50 × 0.35 mm
Theta range for data collection	2.84 to 26.29°
Index ranges	$0 \leq h \leq 22$, $-14 \leq k \leq 0$, $-27 \leq l \leq 25$
Reflections collected	6379
Independent reflections	6181 [R(int)=0.0187]
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	6179/0/407
Goodness-of-fit on F ²	1.038
Final R indices [I > 2σ(I)]	$R_1 = 0.0542$, $wR_2 = 0.1206$
R indices (all data)	$R_1 = 0.0595$, $wR_2 = 0.1253$
Largest diff. peak and hole	0.953 and -0.923 e.Å ⁻³

was evaporated *in vacuo* to give reddish brown solid. Recrystallization of the crude product from a solvent pair of toluene-hexane affords reddish brown crystals in 85% yield.

Analysis: Calcd. (%) C; 29.14, H; 4.61 Found (%) C; 29.04, H; 4.56.

¹H NMR (C_6D_6): δ 5.35 (s, C_5H_5 , 5H), δ 3.58 (m, $(\text{H}_3\text{CO})\text{P}(\text{O})_2$, 6H)

X-ray crystallographic analysis. A X-ray quality single crystal, 0.50 × 0.50 × 0.35 mm, was mounted in a thin-walled glass capillary on an Enraf-Nonius CAD-4 diffractometer with Mo-K α radiation ($\lambda = 0.71073$ Å), unit cell parameters were determined by least-squares analysis of 25 reflections ($10^\circ < \theta < 13^\circ$). Intensity data were collected with θ range of 2.84-26.29° in $\omega/2\theta$ scan mode. Three standard reflections were monitored every 1 hr during data collection. The data were corrected for Lorentz-polarization effects and decay. Empirical absorption corrections with Ψ scans were applied to the data. The structure was solved by using Patterson method and refined by full-matrix least-squares techniques on F² using SHELXS-86⁸ and SHELXL-93.⁹ All non-hydrogen atoms except disordered atoms [O(15) and O(15'), O(16) and O(16'), 3 Cp rings] which were refined isotropically with site occupancies of 0.6 and 0.4, were refined by using anisotropic thermal factors, and all hydrogen atoms were positioned geometrically and refined using riding model. The