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Studies on Ketene and Its Derivatives. CVII.[1] Photoreaction of Diketene with 6-Methyluracil

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Photoreaction of diketene with 6-methyluracil gives *rel*-(1*R*,6*R*,8*S*)-1-methyl-3,5-dioxo-2,4-diazabicyclo[4.2.0]octane-8-spiro-2′-(oxetan)-4′-one (**10a**), *rel*-(1*R*,6*R*,8*R*)-1-methyl-3,5-dioxo-2,4-diazabicyclo[4.2.0]octane-8-spiro-2′-(oxetan)-4′-one (**10b**), *rel*-(1*R*,6*R*,7*S*)-1-methyl-3,5-dioxo-2,4-diazabicyclo[4.2.0]octane-7-spiro-2′-(oxetan)-4′-one (**10c**), and *rel*-(1*R*,6*R*,7*R*)-1-methyl-3,5-dioxo-2,4-diazabicyclo[4.2.0]octane-7-spiro-2′-(oxetan)-4′-one (**10d**). Heating of compounds **10a** and **10b** at their decomposition points results in decarboxylation to give *rel*-(1*R*,6*R*)-1-methyl-8-methylene-3,5-dioxo-2,4-diazabicyclo[4.2.0]octane (**11**). Similarly, thermolysis of **10c** and **10d** affords *rel*-(1*R*,6*S*)-1-methyl-7-methylene-3,5-dioxo-2,4-diazabicyclo[4.2.0]octane (**12**).

Surtcture assignments of **10b** and **10c** by X-ray crystallographic analysis are described. The structures were solved by the direct method and refined to R values of 4.81% for **10b** and 6.79% for **10c**.

Keywords——diketene; 6-methyluracil; photoreaction; [2+2]cycloaddition; spiro-oxetanones; X-ray analysis

During the course of investigation of cycloaddition of the C–C double bond of diketene,[2] we studied the photoreactions of diketene with olefinic compounds such as cyclohexenones **1**,[3] maleic anhydrides **4** (X=O),[4] and maleimides **4** (X=NR′)[1] to give the [2+2] cycloadducts **2**, **3**, and **5**. In addition, photoreaction of uracil with olefin was reported to give a [2+2]-cycloadduct.[5] Recently, Matsuura *et al.*[6] reported that photoreaction of 6-cyano-1,3-dimethyluracil (**6**) with vinyl acetate gave the diazabicyclo[4.2.0]octane (**7**) and 5-(2-cyano-2-acetoxyethyl)uracil (**8**). In the present paper we describe the photolysis of diketene with 6-methyluracil to give [2+2]cycloadducts.

When a solution of diketene and 6-methyluracil (**9**) in aqueous acetone was irradiated, four crystalline products **10a**—**10d** were obtained. Elemental analyses indicated that they were 1:1 adducts of uracil and diketene, and infrared (IR) spectra showed the existence of a β-lactone carbonyl at around 1840 cm^{-1} (**10a**, 1840; **10b**, 1845; **10c**, 1840; **10d**, 1830) indicating that the oxetanone ring remained intact. These observations favored diazabicyclo[4.2.0]-octane-spiro-oxetanone structures for these adducts. We assigned the structures *rel*-(1*R*,6*R*,8*S*)-1-methyl-3,5-dioxo-2,4-diazabicyclo[4.2.0]octane-8-spiro-2′-(oxetan)-4′-one (**10a**), *rel*-(1*R*,6*R*,8*R*)-1-methyl-3,5-dioxo-2,4-diazabicyclo[4.2.0]octane-8-spiro-2′-(oxetan)-4′-one (**10b**), *rel*-(1*R*,6*R*,7*S*)-1-methyl-3,5-dioxo-2,4-diazabicyclo[4.2.0]octane-7-spiro-2′-(oxetan)-4′-one (**10c**), and *rel*-(1*R*,6*R*,7*R*)-1-methyl-3,5-dioxo-2,4-diazabicyclo[4.2.0]octane-7-spiro-2′-(oxetan)-4′-one (**10d**) to these products on the basis of the following results.

Namely, as reported previously, the C_1—C_6 juncture is much more stable in the *cis* configuration, and we initially presumed that these four products exist in the *cis* configuration. In fact, the angular methyl protons of *cis* bicyclo[4.2.0]octanone are reported to appear at lower field (>1.20 ppm) in the proton nuclear magnetic resonance (H^1-NMR) spectrum, while those of the *trans* isomer appear at higher field (<1.00 ppm).[7] The chemical shifts of the C_1-methyl protons of these products appeared at 1.7—1.8 ppm (**10a**, 1.78; **10b**, 1.76; **10c**, 1.80; **10d**, 1.70). These results are consistent with the *cis* structure.

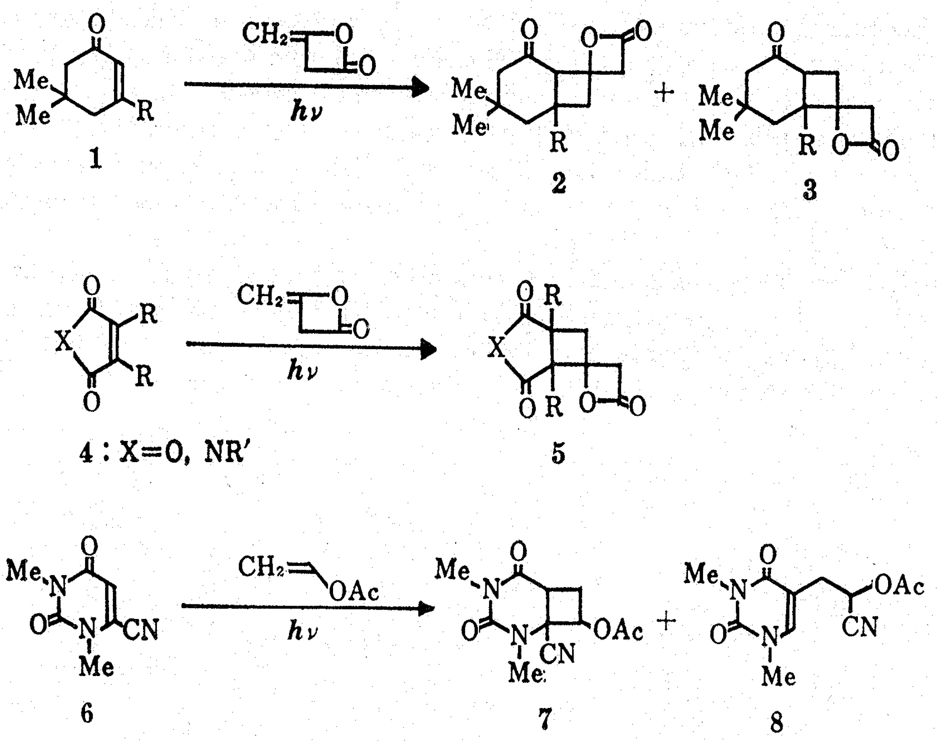


Chart 1

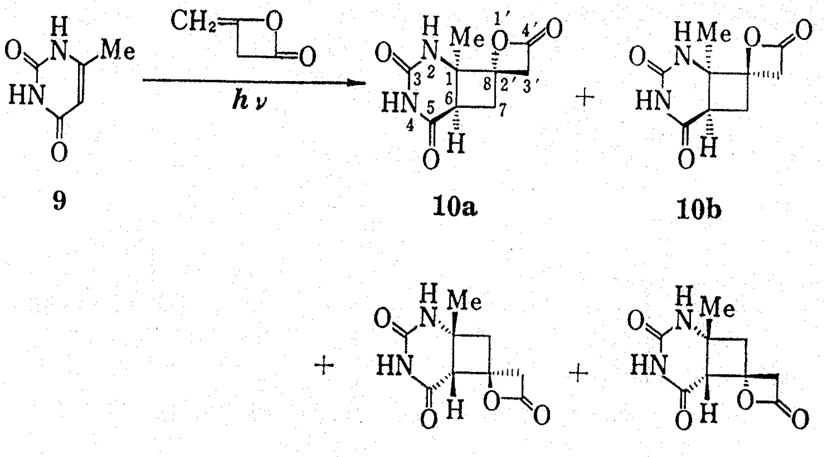


Chart 2

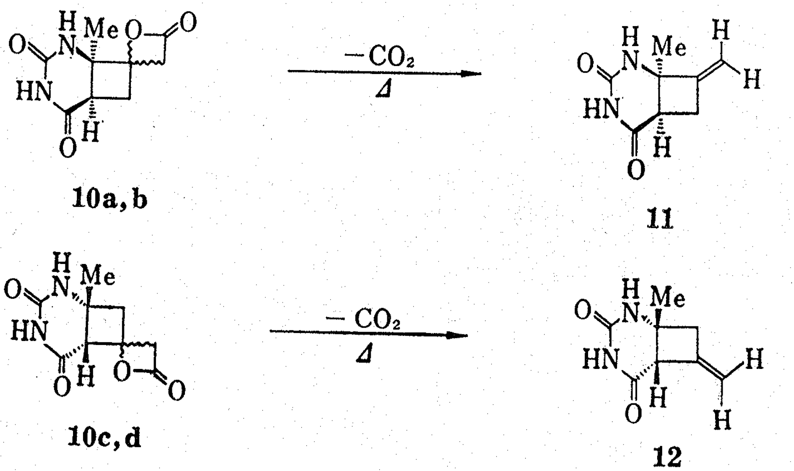


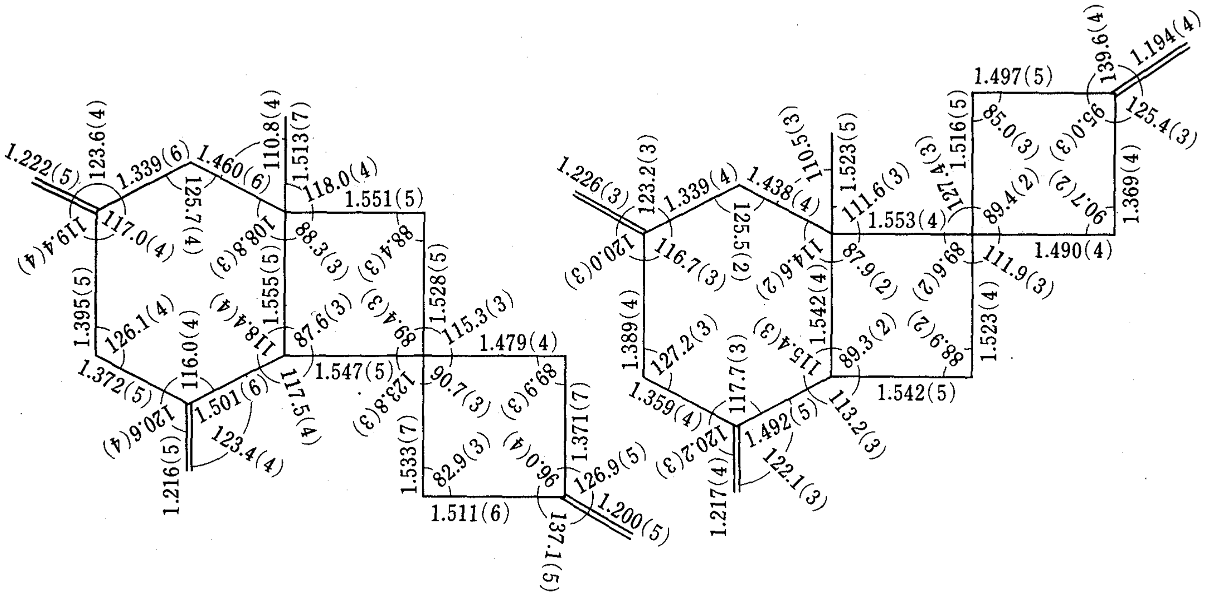
Chart 3

The C_6 methine protons of **10a** and **10b** each appeared as a multiplet signal, while those of **10c** and **10d** appeared as simpler peaks. Therefore, the spiro-carbons of **10a** and **10b** should be the C_8 carbon, and those of **10c** and **10d** should be the C_7 carbon.

Heating of **10a** resulted in decarboxylation to give *rel*-(1*R*, 6*R*)-1-methyl-8-methylene-3,5-dioxo-2,4-diazabicyclo[4.2.0]octane (**11**), which was also obtained from compound **10b** on similar treatment. The isomeric 7-methylene derivative **12** was obtained from both **10c** and **10d**.

These results are also consistent with the indicated structures of **10a**—**10d**. However, the configurations of the C_8 junction of **10a** and **10b** and the C_7 junction of **10c** and **10d** could not be determined, and X-ray analyses of **10b** and **10c** were therefore carried out.

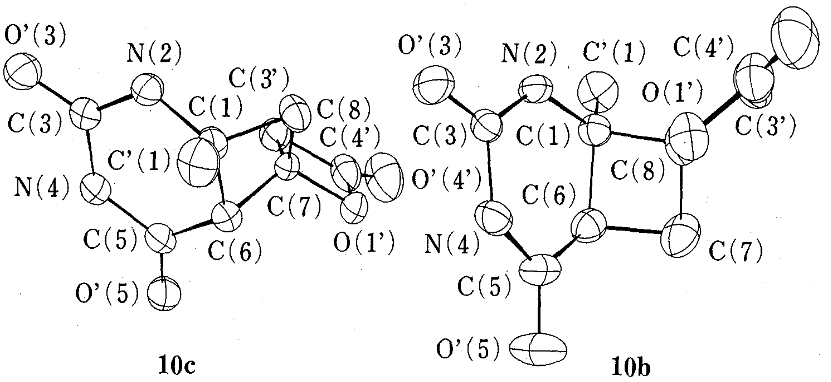
The bond lengths and angles of **10b** and **10c** are shown in Fig. 1.



10c		10b	
N(2)–C(1)–C(8)	110.7(3)	N(2)–C(1)–C(8)	117.3(2)
C(6)–C(1)–C(1)	118.3(4)	C(6)–C(1)–C(1)	113.5(3)
C(8)–C(7)–C(3′)	123.1(4)	O(1)–C(8)–C(1)	112.4(2)
C(6)–C(7)–O(1′)	117.1(3)	C(7)–C(8)–C(3′)	127.0(3)

Fig. 1. Bond Lengths (Å) and Angles(°) of **10b** and **10c**

Compounds **10b** and **10c** show almost the same bond lengths and angles, but the lactone ring binds to the C-8 position in **10b** and the C-7 position in **10c**. A projection of the molecular structure is shown in Fig. 2.



10c **10b**

Fig. 2. Molecular Structures of **10b** and **10c**

Table I. Dihedral Angles between the Least-Squares Planes of **10b** and **10c**

A-Ring : C(1), N(2), C(3), N(4), C(5), C(6)
B-Ring : C(1), C(6), C(7), C(8)
C-Ring : C(1'), C(8) or C(7), C(3'), C(4')

	10b	**10c**
A-Ring—B-ring	114.1°	116.6°
B-Ring—C-ring	90.0	90.0
A-Ring—C-ring	119.6	110.8

The dihedral angles between the least-squares planes of **10b** and **10c** were almost the same, as shown in Table I.

Though **10b** and **10c** have the same space group, their packing properties are different. As a result, a proton-donor or proton-acceptor group of **10b** is involved in a hydrogen bond. As can be seen in Fig. 3, there are two intermolecular hydrogen bonds, N(4)-O'(3) and N(2)-O'(5) (Table II). The hydrogen bonding between N(4) and O'(3) is a dimeric type, like that of a carboxylic acid group, but that between N(2) and O'(5) forms a chain extending along the c-axis.

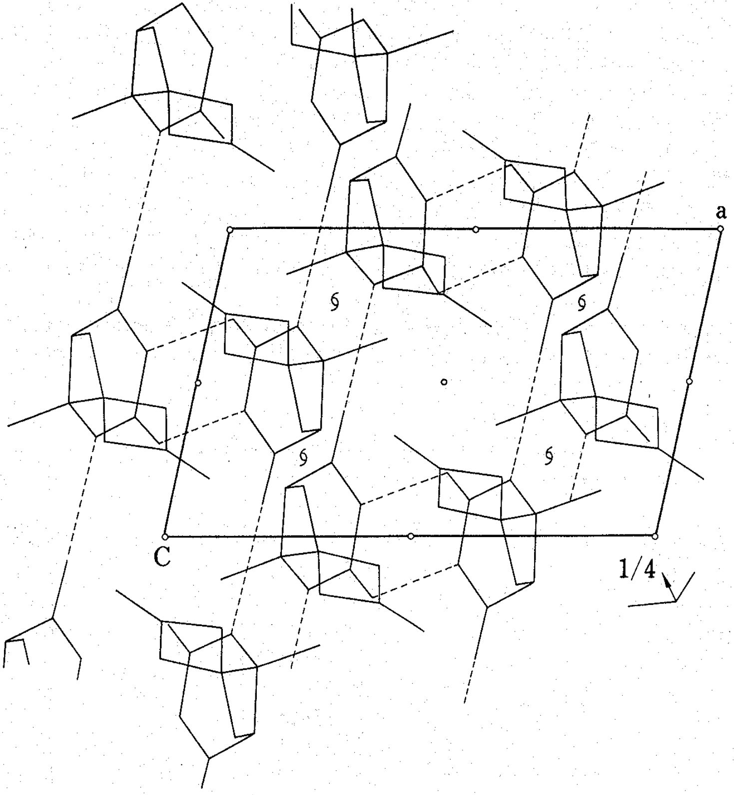


Fig. 3. Crystal Structure of **10b** Viewed along the b-Axis

Table II. Hydrogen Bonds in **10b**

Donor	Acceptor	Coordinates of acceptor	N···O	N···H	H···O	<N-H···O
N(2)	0'(5)	*x*, *y*, *z*-1	2.860(3)Å	0.78(3)Å	2.08(3)Å	172(3)°
N(4)	0'(3)	-*x*,-*y*, 1-*z*	2.922(4)	0.82(3)	2.10(3)	173(3)

Experimental

Melting points are uncorrected. IR spectra were taken on a JASCO IR-S spectrometer. H^1-NMR spectra were recorded on a JEOL JNM-XL 200 machine (for **10a**, **10b**, **10c**, and **10d**) with tetramethylsilane as an internal standard, and on a JEOL JNM-PMX 60 machine (for **11** and **12**) with 3-(trimethylsilyl)propanesulfonic acid sodium salt as an internal standard. The abbreviations used are as follows: s, singlet; d, doublet; dd, double-doublet; t, triplet; q, quartet; m, multiplet; br, broad. High pressure liquid chromatography (HPLC) was carried out on a Waters Associates R-400 series instrument. (Pump: M 6000. Injector: U6K. Packing: μ porasil. Column: 3.9 mm × 30 cm. Solvent: cyclohexane–dioxane (6: 4). Flow rate: 2 ml/min. Detector: UV 254 nm.) The ultraviolet (UV) light source was a Riko UVL-400HA water-cooled high pressure mercury lamp (Pyrex filter). Thin layer chromatography (TLC) was carried out with Wakogel B-5 and the spots were detected by spraying conc. H_2SO_4 followed by heating.

Reaction of 6-Methyluracil (9) with Diketene——A solution of diketene (8.4 g, 0.1 mol) and **9** (1.26 g, 0.01 mol) in acetone–water (4: 1) (150 ml) was irradiated under ice cooling for 7 h. After removal of the solvent and excess diketene under reduced pressure, the resulting crude crystalline substance[8] was recrystallized from EtOH to give 264 mg (13%) of *rel*-(1*R*,6*R*,8*S*)-1-methyl-3,5-dioxo-2,4-diazabicyclo[4.2.0]octane-8-spiro-2′-(oxetan)-4′-one (**10a**) as prisms, 95 mg (5%) of *rel*-(1*R*,6*R*,8*R*)-1-methyl-3,5-dioxo-2,4-diazabicyclo-[4.2.0]octane-8-spiro-2′-(oxetan)-4′-one (**10b**) as prisms, 45 mg (2%) of *rel*-(1*R*,6*R*,7*S*)-1-methyl-3,5-dioxo-2,4-diazabicyclo[4.2.0]octane-7-spiro-2′-(oxetan)-4′-one (**10c**) as prisms, and 29 mg (1%) of *rel*-(1*R*,6*R*,7*R*)-1-methyl-3,5-dioxo-2,4-diazabicyclo[4.2.0]octane-7-spiro-2′-(oxetan)-4′-one (**10d**) as prisms. **10a**: mp 220°C (dec.). *Anal.* Calcd for $C_9H_{10}N_2O_4$: C, 51.42; H, 4.80; N, 13.33. Found: C, 51.38; H, 4.81; N, 13.37. IR ν_{max}^{KBr} cm^{-1}: 3240, 1840, 1720, 1680. H^1-NMR (CF_3CO_2D) δ: 1.78 (3H, s, CH_3), 2.94 (1H, dd, $J=4$ Hz, $J=13$ Hz, C_7–H), 3.21—3.42 (1H, m, C_6–H), 3.42 (1H, dd, $J=4$ Hz, $J=13$ Hz, C_7–H), 3.63 (1H, ABq, $J=18$ Hz, C_3'–H), 3.90 (1H, ABq, $J=18$ Hz, C_3'–H). **10b**: mp 198°C (dec.). *Anal.* Calcd for $C_9H_{10}N_2O_4$: C, 51.42; H, 4.80; N, 13.33. Found: C, 51.29; H, 4.73; N, 13.31. IR ν_{max}^{KBr} cm^{-1}: 3320, 1845, 1690. H^1-NMR (CF_3CO_2D) δ: 1.76 (3H, s, CH_3), 3.00 (1H, dd, $J=6$ Hz, $J=14$ Hz, C_7–H), 3.16—3.34 (1H, m, C_6–H), 3.40 (1H, dd, $J=6$ Hz, $J=14$ Hz, C_7–H), 3.54 (1H, ABq, $J=18$ Hz, C_3'–H), 3.80 (1H, ABq, $J=18$ Hz, C_3'–H). **10c**: mp 183°C (dec.). *Anal.* Calcd for $C_9H_{10}N_2O_4$: C, 51.42; H, 4.80; N, 13.33. Found: C, 51.40; H, 4.85; N, 13.31. IR ν_{max}^{KBr} cm^{-1}: 3400, 1840, 1685. H^1-NMR (CF_3CO_2D) δ: 1.80 (3H, s, CH_3), 3.04 (1H, ABq, $J=14$ Hz, C_8–H), 3.11 (1H, ABq, $J=14$ Hz, C_8–H), 3.65 (1H, ABq, $J=18$ Hz, C_3'–H), 3.89 (1H, d, $J=3$ Hz, C_6–H), 3.99 (1H, ABq, $J=18$ Hz, C_3'–H). **10d**: mp 183°C (dec.). *Anal.* Calcd for $C_9H_{10}N_2O_4$: C, 51.42; H, 4.80; N, 13.33. Found: C, 51.22; H, 4.72; N, 13.24. IR ν_{max}^{KBr} cm^{-1}: 3280, 1830, 1700. H^1-NMR (CF_3CO_2D) δ: 1.70 (3H, s, CH_3), 3.02 (1H, ABq, $J=14$ Hz, C_8–H), 3.10 (1H, ABq, $J=14$ Hz, C_8–H), 3.80 (1H, ABq, $J=18$ Hz, C_3'–H), 3.96 (1H, s, C_6–H), 3.97 (1H, ABq, $J=18$ Hz, C_3'–H).

***rel*-(1*R*,6*R*)-1-Methyl-8-methylene-3,5-dioxo-2,4-diazabicyclo[4.2.0]octane (11)**——a) Compound **10a** (105 mg, 0.5 mmol) was heated on a silicone oil bath at 230°C for 5 min. When the evolution of gas had

TABLE III. Crystal Data for **10b** and **10c**

		10b	10c
Molecular formula		$C_9H_{10}N_2O_4$	$C_9H_{10}N_2O_4$
Molecular weight		210.189	210.189
Crystal system		Monoclinic	Monoclinic
Lattice constants	a	11.1272(5) Å	11.9664(6) Å
	b	12.8247(7) Å	6.8187(4) Å
	c	6.8881(3) Å	13.2369(6) Å
	β	103.044(4)°	115.494(5)°
	v	957.5893 Å^3	974.9062 Å^3
Systematic absences		h01 : h+1 odd	h01 : h+1 odd
		h00 : (h odd)	h00 : (h odd)
		001 : (1 odd)	001 : (1 odd)
		0k0 : k odd	0k0 : k odd
Space group		$P2_1/n$	$P2_1/n$
Number of molecules in a unit cell		$Z=4$	$Z=4$
Calculated density		1.458 g/cm^3	1.432 g/cm^3
Observed density		1.451 g/cm^3	1.434 g/cm^3
Radiation used		Cu $K\alpha$	Cu $K\alpha$
Theta range		$3<\theta<78°$	$3<\theta<78°$
No. of obsd. reflections		1256	1775

ceased, the residue was recrystallized from benzene to give the product **11** as prisms, mp 201—202°C. Yield, 46 mg (55%). *Anal.* Calcd for $C_8H_{10}N_2O_2$: C, 57.82; H, 6.07; N, 16.86. Found: C, 57.57; H, 6.11; N, 17.13. IR ν_{max}^{KBr} cm^{-1}: 3200, 1710, 1685, 1450. H^1-NMR (CF_3CO_2H) δ: 1.60 (3H, s, CH_3), 2.82—3.55 (3H, m, C_6–H, C_7–H), 4.95—5.35 (2H, m, *exo*-methylene), 7.33—7.72 (1H, br, NH), 9.22—9.80 (1H, br, NH).

b) Compound **10b** (105 mg, 0.5 mmol) was heated on a silicone oil bath at 205°C for 7 min. The residue was purified by recrystallization from benzene to give the product **11**. Yield, 60 mg (72%).

***rel*-(1*R*,6*S*)-1-Methyl-7-methylene-3,5-dioxo-2,4-diazabicyclo[4.2.0]octane** (**12**)——a) Compound **10c** (105 mg, 0.5 mmol) was heated on a silicone oil bath at 190°C for 10 min. The residue was purified by recrystallization from benzene to give **12** as prisms, mp 190—191°C. Yield, 53 mg (64%). *Anal.* Calcd for $C_8H_{10}N_2O_2$: C, 57.82; H, 6.07; N, 16.86. Found: C, 58.05; H, 6.11; N, 17.08. IR ν_{max}^{KBr} cm^{-1}: 3200, 1690, 1670, 1455. H^1-NMR (CF_3CO_2H) δ: 1.62 (3H, s, CH_3), 3.03 (2H, t, $J=2$ Hz, C_8–H), 3.86 (1H, d, $J=2$ Hz, C_6–H), 5.00—5.43 (2H, m, *exo*-methylene), 7.30—7.67 (1H, br, NH), 9.13—9.67 (1H, br, NH).

b) Compound **10d** (21 mg, 0.1 mmol) was heated on a silicone oil bath at 190°C for 10 min. The residue was purified by recrystallization from benzene to give the product **12**. Yield, 11 mg (66%).

X-Ray Analysis of 10b and 10c——The crystals were grown in EtOH solutions as colorless prisms. A computer-controlled Philips PW 1100 four-circle X-ray auto diffractometer was used for all measurements. The unit cell dimensions and orientation matrix were derived from a least-squares fit of the angular values of 20 reflections. The crystal data for **10b** and **10c** are given in Table III.

The intensities of all the reflections in the appropriate 2θ range were measured using a variable speed θ-2θ scan technique. The scan speed was 4°/min for all reflections. The total number of reflections measured in each case is given in Table III.

The structures of both adducts were solved by the direct method using MULTAN[9] and refined by the block-diagonal least-squares procedure. A difference Fourier synthesis was used to locate the hydrogen atoms in both compounds. R was reduced to 4.81% for **10b** and to 6.79% for **10c** after several cycles of

TABLE IV. Positional Parameters and Thermal Parameters of **10b** with Their Estimated Standard Deviations in Parentheses

	x	y'	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	2483(3)	2624(2)	4295(4)	51(2)	38(2)	129(6)	−4(2)	18(3)	−2(3)
N(2)	1772(2)	1792(2)	3197(3)	67(2)	38(2)	100(5)	−9(2)	28(3)	−3(2)
C(3)	1071(3)	1116(2)	3930(4)	56(2)	34(2)	116(6)	7(2)	23(3)	8(3)
N(4)	1119(2)	1177(2)	5960(4)	63(2)	45(2)	128(6)	−6(2)	30(3)	9(3)
C(5)	1871(3)	1793(3)	7319(4)	60(3)	60(2)	109(6)	7(2)	19(3)	3(3)
C(6)	2720(3)	2515(2)	6579(4)	51(2)	46(2)	130(7)	1(2)	4(3)	−10(3)
C(7)	2377(3)	3674(3)	6717(5)	77(3)	53(2)	194(8)	−1(2)	−6(4)	−31(4)
C(8)	1798(3)	3660(2)	4491(5)	50(3)	35(2)	210(8)	−8(2)	6(4)	−1(3)
O(1')	435(2)	3522(2)	4081(3)	50(2)	41(1)	229(6)	−1(1)	4(3)	4(2)
C(3')	1618(4)	4581(3)	3076(6)	100(4)	43(2)	303(11)	−7(3)	23(5)	27(4)
C(4')	272(3)	4339(3)	2769(6)	82(3)	41(2)	261(10)	8(2)	6(5)	−4(4)
C'(1)	3652(3)	2812(3)	3545(5)	63(3)	66(3)	233(9)	−13(2)	51(4)	−4(4)
O'(3)	429(2)	452(2)	2912(3)	90(2)	46(1)	160(5)	−23(2)	37(3)	−11(2)
O'(5)	1846(2)	1741(2)	9074(3)	117(3)	110(3)	110(5)	−19(2)	36(3)	−2(3)
O'(4')	−697(2)	4637(2)	1808(4)	100(3)	70(2)	360(9)	33(2)	−10(4)	14(4)

	x	y	z	B_{iso}
H(N2)	1730(25)	1747(22)	2050(41)	2.70(64)
H(N4)	704(27)	737(23)	6378(43)	3.20(67)
H(C6)	3557(27)	2351(25)	7238(44)	3.72(74)
H(C7)	1831(30)	3871(26)	7669(48)	4.46(79)
H'(C7)	3026(32)	4129(28)	6975(52)	5.54(91)
H(C3')	1862(25)	4509(22)	1986(40)	2.75(61)
H'(C3')	1839(35)	5337(31)	3737(57)	6.55(102)
H(C'1)	4155(30)	2177(26)	3796(48)	4.54(80)
H'(C'1)	3469(34)	2980(29)	2093(54)	5.71(98)
H''(C'1)	4099(28)	3390(25)	4297(46)	3.95(75)

For non-hydrogen atoms, $T=\exp[-\beta_{11}h^2+\cdots+2\beta_{23}kl)]$; all quantities are $\times 10^4$
For hydrogen atoms, $T=\exp[-B_{iso}\sin^2\theta/\lambda^2]$; fractional coordinates are $\times 10^4$

Table V. Positional Parameters and Thermal Parameters of **10c** with their Estimated Standard Deviations in Parentheses

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	7877(3)	862(6)	1021(3)	52(3)	126(9)	45(3)	−15(4)	21(2)	−5(4)
N(2)	9067(3)	1010(5)	970(3)	48(3)	135(8)	66(3)	14(4)	26(2)	31(4)
C(3)	9441(4)	2558(6)	574(3)	55(3)	114(9)	53(3)	6(4)	23(2)	6(4)
N(4)	8225(3)	3826(5)	−135(3)	49(3)	113(7)	65(3)	0(4)	18(2)	20(4)
C(5)	7272(4)	3603(6)	−496(4)	57(4)	92(8)	68(3)	−3(4)	12(3)	−2(4)
C(6)	6875(3)	1918(6)	3(3)	46(3)	104(8)	59(3)	−4(4)	17(2)	−7(4)
C(7)	6600(3)	−58(6)	−631(3)	35(3)	102(8)	50(3)	−7(4)	8(2)	−1(4)
C(8)	7236(4)	−1130(6)	486(3)	70(4)	108(9)	48(3)	−15(5)	13(3)	5(4)
O(1')	5284(2)	−570(4)	−1304(3)	40(2)	160(7)	75(3)	−21(3)	6(2)	−4(3)
C(3')	6888(4)	−472(6)	−1633(3)	60(4)	150(10)	48(3)	−4(5)	15(3)	−2(4)
C(4')	5548(4)	−1104(7)	−2177(4)	75(4)	142(10)	63(3)	−22(5)	−9(3)	16(5)
C'(1)	8000(5)	1323(8)	2179(4)	91(5)	251(13)	55(3)	−37(7)	36(3)	−33(5)
O'(3)	10523(3)	2874(5)	779(3)	49(2)	180(8)	92(3)	12(4)	34(2)	46(4)
O'(5)	6549(3)	4712(5)	−1188(3)	63(3)	149(8)	113(3)	5(4)	−1(2)	48(4)
O'(4')	4852(4)	−1846(6)	−3042(3)	135(5)	305(12)	63(3)	−68(6)	−22(3)	−16(5)

	x	y	z	B_{iso}
H(N2)	9600(46)	311(81)	1183(42)	5.45(130)
H(N4)	8874(38)	4850(67)	−424(35)	3.59(98)
H(C6)	6031(41)	2336(71)	244(37)	4.18(107)
H(C8)	7675(38)	−2046(66)	515(34)	3.36(96)
H'(C8)	6468(41)	−1522(71)	799(37)	4.33(108)
H(C3')	7560(41)	−1424(71)	−1605(37)	4.19(108)
H'(C3')	7136(37)	708(63)	−2019(33)	3.11(92)
H(C'1)	8493(42)	305(72)	2774(38)	4.52(110)
H'(C'1)	7188(39)	1137(67)	2184(34)	3.62(101)
H''(C'1)	8200(46)	2614(81)	2398(42)	5.69(130)

For non-hydrogen atoms, $T=\exp[-\beta_{11}h^2+\cdots+2\beta_{23}kl)]$; all quantities are $\times 10^4$
For hydrogen atoms, $T=\exp[-B_{iso}\sin^2\theta/\lambda^2]$; fractional coordinates are $\times 10^4$

least-squares calculation assuming anisotropic thermal parameters for the non-hydrogen atoms and isotropic ones for the hydrogen atoms. The final positional and thermal parameters are given in Tables IV and V. The atomic scattering factors for carbon and oxygen were from the International Tables for X-Ray Crystallography,[10] and for hydrogen, from Stewart *et al.*[11]

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