Crystal Structure of 5-(4-Bromophenyl)-4-cyano-4'-phenyl-spiro[2H-pyran-2, 1'-cyclohexane]-3(6H)-one

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The chemistry of 2-pyrones began about one hundred years ago, and attracted much attention after some 2-pyrone derivatives were found in naturally occurring materials. Many steroids showing cardiac activity contain a 2-pyrone side-chain, for example.¹ Therefore, many preparative methods and structural features of α -pyrones have been investigated.² During the course of our investigations concerning the nucleophilic reactivity of alkylidenecyanoalkenoates, we found a simple preparative method of spiro lactone.² Carbon nucleophile generated from alkylidenecyanoalkenoates with alkoxide ion attacked carbonyl carbon to give 1,4-cycloaddition products. Here, we report the crystal structure of a spiro lactone, **3** (R=Ph, Ar=4-bromophenyl), shown in Fig. 1. The spiro lactone, **3**, was prepared by a condensation reaction of cyanoalkenoate, **2**, with cyclohexanones (7% yield).³ The material had good crystallinity and could be

identified by the usual spectroscopy and elemental analysis. Single crystals of the spiro lactone, **3**, were obtained using a mixed solvent of CCl₄ and CHCl₃ (2 : 1). Reflection data were collected on a Rigaku AFC7R diffractometer using Mo K α monochromated with graphite at room temperature as summarized in Table 1 and corrected for Lorentz and polarization effects. The structure was solved by a direct method (SIR 92), and refined by full-matrix least-squares with anisotropic thermal parameters for the non-hydrogen atoms. In a later stage of the refinement, reflection data were corrected for absorption and

Fig. 1 Reaction scheme to form **3**.

Table 1 Crystal and experimental data for spiro lactone, **3**

Formula: C ₂₂ H ₂₀ NO ₂ Br	
Formula weight = 422.32	
Crystal system: monoclinic	
Space group: P2 ₁ /c (#14)	Z = 4
a = 8.085(3) Å	
b = 23.808(2) Å	β = 90.75(3)°
c = 10.222(3) Å	
V = 1967.5(8) Å ³	
D _x = 1.43 g/cm ³	
No. observed reflections: 2770	
2 θ range: 6 – 60° with Mo K α	
Scan type: $\theta/2\theta$	
Scan speed = 16°/min	
F(0 0 0) = 864	
μ (Mo K α) = 21.13/cm	
R = 0.039, R _w = 0.038	
Goodness-of-fit indicator = 1.70	
($\Delta\rho$) _{max} = 0.02	
($\Delta\rho$) _{max} = 0.47 eÅ ⁻³	
($\Delta\rho$) _{min} = -0.46 eÅ ⁻³	

Table 2 Positional parameters and B_{eq} for spiro lactone, **3**

Atom	x	y	z	B _{eq}
Br	0.10911(5)	0.35269(1)	0.19331(4)	5.00(1)
O(1)	0.0922(2)	-0.01936(8)	0.3334(2)	3.09(5)
O(2)	-0.1772(3)	-0.01980(9)	0.3570(3)	4.32(6)
N	-0.3523(4)	0.1090(1)	0.3154(4)	5.63(9)
C(1)	-0.0537(4)	0.0069(1)	0.3349(3)	2.98(7)
C(2)	-0.0577(4)	0.0683(1)	0.3115(3)	2.84(7)
C(3)	0.0809(4)	0.0995(1)	0.3060(3)	2.71(7)
C(4)	0.2418(4)	0.0700(1)	0.3316(4)	3.18(8)
C(5)	0.2410(4)	0.0094(1)	0.2842(3)	2.87(7)
C(6)	0.2384(5)	0.0044(1)	0.1359(4)	3.60(9)
C(7)	0.2460(5)	-0.0562(2)	0.0884(4)	3.83(10)
C(8)	0.3953(5)	-0.0877(1)	0.1467(4)	3.90(9)
C(9)	0.3931(5)	-0.0838(1)	0.2949(4)	3.69(9)
C(10)	0.3849(4)	-0.0234(1)	0.3436(4)	3.30(9)
C(11)	-0.2215(4)	0.0919(1)	0.3107(4)	3.67(9)
C(12)	0.0833(4)	0.1606(1)	0.2793(3)	2.69(7)
C(13)	-0.0124(4)	0.1839(1)	0.1804(4)	3.46(8)
C(14)	-0.0032(4)	0.2407(2)	0.1526(4)	3.93(9)
C(15)	0.0978(4)	0.2744(1)	0.2275(3)	3.28(8)
C(16)	0.1939(5)	0.2526(1)	0.3257(4)	3.76(9)
C(17)	0.1890(4)	0.1951(1)	0.3497(4)	3.54(9)
C(18)	0.4058(4)	-0.1467(1)	0.0928(3)	3.30(8)
C(19)	0.3311(5)	-0.1923(2)	0.1511(4)	4.3(1)
C(20)	0.3435(6)	-0.2454(2)	0.1000(5)	4.8(1)
C(21)	0.4275(5)	-0.2539(2)	-0.0131(5)	5.0(1)
C(22)	0.4990(6)	-0.2097(2)	-0.0743(5)	5.7(1)
C(23)	0.4905(5)	-0.1565(2)	-0.0208(4)	4.7(1)

$$B_{eq} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$$

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Table 3 Bond distances(Å) and angles(°) of **3**

atom	atom	distance	atom	atom	distance
Br	C(15)	1.899(3)	O(1)	C(1)	1.335(3)
O(1)	C(5)	1.479(3)	O(2)	C(1)	1.207(3)
N	C(11)	1.134(4)	C(1)	C(2)	1.482(4)
C(12)	C(17)	1.382(4)	C(2)	C(3)	1.346(4)
C(2)	C(11)	1.438(4)	C(3)	C(4)	1.498(4)
C(3)	C(12)	1.480(4)	C(4)	C(5)	1.522(4)
C(5)	C(6)	1.520(5)	C(5)	C(10)	1.522(4)
C(6)	C(7)	1.523(5)	C(7)	C(8)	1.535(5)
C(8)	C(9)	1.518(5)	C(8)	C(18)	1.511(5)
C(9)	C(10)	1.523(5)			

atom	atom	atom	angle	atom	atom	atom	angle
C(1)	O(1)	C(5)	120.7(2)	O(1)	C(1)	O(2)	119.3(3)
O(1)	C(1)	C(2)	118.5(3)	C(6)	C(7)	C(8)	112.0(3)
O(2)	C(1)	C(2)	122.2(3)	C(1)	C(2)	C(3)	122.3(3)
C(1)	C(2)	C(11)	113.9(3)	C(3)	C(2)	C(11)	123.5(3)
C(2)	C(3)	C(4)	117.2(3)	C(2)	C(3)	C(12)	124.2(3)
C(7)	C(8)	C(9)	109.8(3)	C(4)	C(3)	C(12)	118.6(3)
C(7)	C(8)	C(18)	111.2(3)	C(3)	C(4)	C(5)	112.8(3)
C(9)	C(8)	C(18)	115.0(3)	C(8)	C(9)	C(10)	112.7(3)
O(1)	C(5)	C(4)	109.3(2)	O(1)	C(5)	C(6)	107.6(3)
O(1)	C(5)	C(10)	104.3(3)	C(4)	C(5)	C(6)	113.1(3)
C(4)	C(5)	C(10)	111.1(3)	C(5)	C(10)	C(9)	113.0(3)
C(6)	C(5)	C(10)	111.0(3)	C(5)	C(6)	C(7)	113.1(3)
N	C(11)	C(2)	176.6(4)	C(3)	C(12)	C(13)	121.5(3)
C(3)	C(12)	C(17)	119.9(3)	Br	C(15)	C(14)	120.1(3)
Br	C(15)	C(16)	118.7(3)	C(12)	C(17)	C(16)	120.8(4)

extinction. All of the calculations were performed using the program system (teXsan) on the SGI Indy computer of Center for Instrumental Analysis of Ibaraki University. The final results of refinement and the atomic coordinates are shown in Tables 1 and 2, respectively. The bond distances and angles of the 2-pyrone and cyclohexane part are listed in Table 3. ORTEP drawing of **3** is shown in Fig. 2. Eight relatively large

Fig. 2 ORTEP drawing of **3** with atom labeling.

electron density peaks (0.47 – 0.23) were observed in the final difference Fourier map around the bromine atom. We assumed that they were electron density peaks of the bromine atom due to the thermal motion of the atom.

The phenyl group on the cyclohexane ring adopts equatorial position which is favorably positioned at least in the cyclohexane part. The stereoselective nucleophilic attack to the carbonyl group resulted in one geometrical isomer, in which the carbon-oxygen of lactone ring is *cis* to the phenyl group. Consequently, 1,4-addition occurred.

References

1. R. Livingston, "Chemistry of Carbon Compounds", ed. S. Coffey, **1977**, Vol. IV Elsevier Scientific Publishing Company, Amsterdam, part E, 10 – 20.
2. G. P. Ellis, "Comprehensive Heterocyclic Chemistry", ed. A. R. Katritzky and C. W. Rees, **1984**, Pergamon Press, Vol. 3, Oxford, 675 – 692.
3. M. Igarashi, Y. Nakano, and M. Yatsu, *Synthesis*, **1984**, 1075.