Department of Applied Chemistry and Fine Chemical Technology, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, P. R. China

J. Froelich, K. Meretter and F. Sauter

Institute of Organic Chemistry, Technical University, Vienna, A-1060 Vienna, Austria

Spiro[5,5]undecane-3-one 1 was converted to 4,7-dihydrospiro[benzo[d]thiazole-6(5H),1'-cyclohexane]-2-amine 3, which is condensed with bromomethyl (halo)phenyl ketones and cyclized to compounds 5a-5c. The X-ray crystallography of the 5b reveals that formation route for 5 is *via* 3-position-substituted-spiro-iminothiazole 4.

J. Heterocyclic Chem., 36, 1307 (1999).

Introduction.

Thiazole and imidazole compounds are intensively studied due to their broad spectrum bioactivity [1,2]. Among them, imidazo[2,1-b]thiazole derivatives are pharmaceutically important because they exhibit anylarthritic [3] antiflammatory [4] and other activities. Considering whether any other derivatives in this class are of pharmaceutical importance, we concentrated on the synthesis of spiroimidazothiazoles. Based on our previously reported systematic research on new spiroheterocyclic system [5-7], we synthesized and charatererized several new hydrogenated spirothiazoles and spiroimidazo[2,1-b]thiazoles which are reported in this paper. One is 2-(p'-chloro)-5,8-dihydrospiro[imidazo[2,1-b]benzo[d]thiazole-7(6H), 1'-cyclohexane] 5b. In theory, there are two possible conversion routes to 5b from 4,7-dihydrospiro[benzo[d]thiazole-6(5H),1'-cyclohexane]-2-amine 3. Determination of the X-ray structure of **5b** confirmed its synthetic route.

Results and Discussion.

Several hydrogenated spiroimidazo[2,1-b]thiazole compounds were synthesized in four steps starting from spiro-[5,5]undecane-3-one 1 (Scheme 1). Compound 1 was prepared by the method published by us [8]. Similar to the preparation of thiazoles and imidazoles [9], compound 1 was treated with thiaurea in the presence of iodine at a temperature of 100° to give 4,7-dihydrospiro[benzo[d]-thiazole-6(5H), 1'-cyclohexane]-2-amine hydroiodide 2. Compound 2 was treated with ammonia solution to give the free spiroaminothiazole 3. Compounds 2 and 3 were both obtained in good yields.

Condensation of compounds 3 with bromomethyl phenyl ketone afforded spirouniothiazole 4a. While with bromomethyl halo-substituted ketones gave analogues 4b-4c.

Cyclization of 4a-4c by refluxing in ethanol was found to proceed effectively to produce spiroimidazo[2,1-b]-thiazoles 5a-5c respectively in good to high yields. These compounds were determined with elemental analysis, ¹H-nmr (Table 1) and ¹³C-nmr (Table 2). ¹H-nmr spectrum

shows the imidazole-ring 3-H protons in the regions d = 7.50-7.55 ppm; 13 C-nmr spectrum shows the imidazole-ring 3-C carbons in the regions d = 105.4-105.6 ppm and the 7-C spirocarbons resonances in the regions d = 33.7-33.8 ppm. The structures of the new compounds 2, 3, 4a-4c and 5a-5c are two new spiro systems which have not yet appeared in literature.

Two ways from spiroaminothiazole 3 to obtain compounds 5a-5c are considered to be possible in theory. The first is that the endo-nitrogen atom of compound 3 attacks the bromomethyl phenyl ketones to give compound 5via compound 4. The second is that the exo-nitrogen atom of compound 3 attacks the bromomethyl phenyl ketone to give structure 6 which is the isomer of 5, where the phenyl group is at the 3-position in the imidazo[2,1-b]thiazole ring. Crystalline 5b (X = Cl) was separated and analyzed by X-ray crystallography. The molecular structure of 5b is

Table 1 1H-NMR Spectroscopic Data for Compound 5

5a	1.40-1.60 (10H, m, Cyclohexane-H), 1.82 (2H, t, J = 6.7 Hz, 6-H), 2.57 (2H, s, 8-H), 2.65 (2H, t, J = 6.7 Hz, 5-H),
	7.55 (1H, s, 3-H), 7.40 (3H, t, J = 7.7 Hz, Phenyl-H), 7.84 (2H, d, Phenyl-H, J = 7.7 Hz)
5b	1.30-1.67 (10H, in, Cyclohexane-H), 1.82 (2H, t, J = 6.7 Hz, 6-H), 2.52 (2H, s, 8-H), 2.60 (2H, t, J = 6.7 Hz, 5-H),
	7.50 (1H, s, 3-H), 7.23 (2H, d, Phenyl-H, J = 7.7 Hz), 7.75 (2H, d, Phenyl-H, J = 7.7 Hz)
5c	130-1.65 (10H, m, Cyclohexane-H), 1.81 (2H, t, J = 6.7 Hz, 6-H), 2.55 (2H, s, 8-H), 2-65 (2H, t, J = 6.7 Hz, 5-H),
	7.51 (1H, s, 3-H), 7.50 (2H, d, Phenyl-H, J = 9.7 Hz), 7.70 (2H, d, Phenyl-H, J = 9.7 Hz)

Table 2

13C-NMR Spectroscopic Data for Compounds 5

Compounds	x		S N	Phenyl-C
5a	Н	19.4 (t), 21.6 (t, 2C), 26.4 (t),	105.4 (d, C-3), 120.6 (s),	124.9 (d, 2C), 126.8 (d),
		32.0 (t), 33.8 (s. C-7), 35.1	124.6 (s), 146.2 (s),	128.4 (d, 2C), 134.4 (s)
		(t, 2C), 35.7 (t)	148.2 (s)	
5b	Cl	19.4 (t), 21.6 (t, 2C), 26.3 (t),	105.6 (d, C-3),120.9 (s),	126.0 (d, 2C),
		32.0 (t), 33.7 (s) 35.0 (t),	124.5 (s), 145.1 (s).	1.28.6 (d, 2C),
		35.7 (t, 2C)	148.4 (s)	132.3 (s), 132.9 (s)
5c	Br	19.4 (t), 21.6 (t, 2 C), 26.3 (t),	105.6 (d), 120.5 (s),	124.5 (s), 126.4
		32.0 (t), 33.8 (t, C-7), 35.1	121.0 (s), 145.2 (s),	(d, 2C), 131.5 (d, 2C),
		(t), 35.7 (t, 2C)	148.5 (s)	133.3 (s),
		19.4 (t), 21.6 (t, 2C), 26.3 (t), 32.0 (t), 33.7 (s) 35.0 (t), 35.7 (t, 2C) 19.4 (t), 21.6 (t, 2 C), 26.3 (t), 32.0 (t), 33.8 (t, C-7), 35.1	105.6 (d, C-3),120.9 (s), 124.5 (s), 145.1 (s). 148.4 (s) 105.6 (d), 120.5 (s), 121.0 (s), 145.2 (s),	1.28.6 (d, 2C), 132.3 (s), 132.9 (s) 124.5 (s), 126.4 (d, 2C), 131.5 (d, 2C),

shown in Figure 1. Final atomic coordinates and isotropic thermal parameters of **5b** are given in Table 3 and bond lengths and bond angles are listed in Table 4.

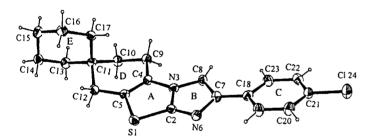


Figure 1. The x-ray crystallographic structure of 5b.

The x-ray crystallography data show that the molecule consists of an essentially planar part formed by the five-membered rings S(1)-C(2)-N(3)-C(4)-C(5) (ring A) and C(2)-N(5)-C(7)- C(8)-N(3) (B), the p-Cl-phenyl moiety (C) and five of the six atoms of ring C(4)-C(5)-C(12)-C(11)-C(10)-C(9) (D). Only the spiro atom C(11) of ring D is distinctly off from this plane (by 0.58A° from the l.s. plane through rings A and B) and constitutes the link to the spiro-6-ring C(11)-C(13)-C(14)-C(15)-C(16)-C(17) (E) which is oriented approximately perpendicular to the planar main part of the molecule. Bond lengths on rings A and B and the trigonal planar coordination of N(3) are consistent with an quasi-aromatic system, although formally only the bonds C(2)-N(6), C(7)-C(8) and C(4)-C(5) are double bonds. Obviously by crystal packing effects is the p-Cl-phenyl moiety twisted by

13.3(1)° (l.s. planes angle) about the C(7)- C(8) bond against the mean plane of ring A and B.

The X-ray crystallography analysis shows that only compound 5 is formed while copound 6 is not detected. In consequence the bromometheyl phenyl ketone is coupled with the endo-nitrogen atom of compound 3; and following cyclisation affords spiroheterocyclic compound 5 via intermediate compound 4 by the first route. So the conversion mechanism shown in Scheme 1 is unambiguously confirmed after verifying the structure of 5b.

EXPERIMENTAL

Spiro[5,5]undecane-3-one 1 was synthesized by the previously described procedure [8].

All melting points were determined on a PHMK microscopic melting point apparatus and are uncorrected. The nmr spectra were measured in tetramethylsilane with a Bruker AC-200 spectrometer. Chemical shifts given are in ppm. Elemental analyses were performed on a Perkin-Elmer 240C instrument.

Crystallography.

A colorless crystal fragment (0.40 x 0.38 x 0.26 mm³), $C_{20}H_{21}ClN_2S$, $M_r=356.91$, monochnic, space group $P2_1/c$, $a=15.278(4)(A^\circ)$, $b=10.823(3))(A^\circ)$, $c=11.383(3)(A^\circ)$, b=111.55(2), V=17.50.7(8) $A^{\circ 3}$, Z=4, $D_C=1.354$ g cm³, T=24C. A Philips PW1100 four-circle diffractometer and graphite monochromatized MoKa radiation, l=0.71069, were used to determine accurate cell dimensions (30 reflections, $q=10^\circ$ to 24°) and to measure 3425 reflections by q-2q scans in the range $q=2^\circ$ to 25, h=-18 to 16, k=0 to 12, and l=0 to 13. Three periodically monitored reference reflections showed fluctuations less then 1%. The data,

Table 3
Final Atomic Coordinates and Isotropic Thermal Parameters of 5b

Table 4
Bond Lengths (A) and Bond Angles (°) of 5b

Final Atomic Coordinates and Isotropic Thermal Parameters of 5b				Bond Lengths (A) and Bond Angles (*) of 50				
Atom	x/a	y /b	z /c	U_{eq} [A°2]	Bond Lengths (A°)			
S(1)	0.25161(5)	-0.02245(7)	0.27849(8)	0.0435(3)	S(1)-C(2)	1.743(3)	C(11)-C(12)	1.545(4)
C(2)	0.3653(2)	0.0273(3)	0.3017(3)	0.036(1)	S(1)-C(5)	1.759(3)	C(11)-C(13)	1.539(5)
N(3)	0.3979(2)	0.1031(2)	0.4042(2)	0.036(1)	C(2)-N(3)	1.362(4)	C(11)-C(17)	1.533(4)
C(4)	0.3346(2)	0.1272(3)	0.4643(3)	0.036(1)	C(2)-N(6)	1-306(5)	C(13)-C(14)	1.524(4)
C(5)	0.2523(2)	0.0691(3)	0.4065(3)	0.038(1)	N(3)-C(4)	1.399(4)	C(14)-C(15)	1.514(5)
N(6)	OA236(2)	0.0135(2)	0.2429(2)	0.040(1)	N(3)-C(8)	1.380(4)	C(15)-C(16)	1.515(6)
C(7)	0.5004(2)	0.0869(3)	0.3125(3)	0.038(1)	C(4)-C(5)	1.342(4)	C(16)-C(17)	1.534(4)
C(8)	0.4857(2)	0.1424(3)	0.4115(3)	0.039(1)	C(4)-C(9)	1.480(4)	C(18)-C(19)	1.398(5)
C(9)	0.3575(2)	0.2070(3)	0.5773(3)	0.043(1)	C(5)-C(12)	1.500(5)	C(18)-C(23)	1.394(4)
C(10)	0-2811(2)	0.1899(3)	0.6338(3)	0.042(1)	N(6)-C(7)	1.397(3)	C(19)-C(20)	1.379(5)
C(11)	0.1795(2)	0.1901(3)	0.5356(3)	0.035(1)	C(7)-C(8)	1.367(5)	C(20)-C(21)	1.381(4)
0(12)	0.1601(2)	0.0702(2)	0.4459(3)	0.040(1)	C(7)-C(18)	1.465(5)	C(21)-C(22)	1.369(5)
C(12)	0.1691(2)	0.0793(3)			C(9)-C(10)	1.536(5)	C(21)-Cl(24)	1.752(4)
C(13)	0.1126(2)	0.1749(3)	0.6080(3)	0.044(1)	C(10)-C(11)	1.544(3)	C(22)-C(21)	1.385(5)
C(14)	0.0094(2)	0.1932(3)	0.5253(3)	0.047(1)	C(10) C(11)	1.5 (((5)	0(22) 0(21)	-10-10(0)
C(15)	-0.0054(2)	0.3202(3)	0.4654(3) 0.3856(3)	0.053(2)		Bond A	ngles (°)	
C(16)	0.0546(2)	0.3344(3)	0.3830(3)	0.049(1) 0.041(1)				
C(17)	0.1590(2)	0.3133(3)		0.041(1)	C(2)-S(1)-C(5)	89.9(1)	C(10)-C(11)-C(113)	107.5(2)
C(18)	0.5805(2)	0.1019(3)	0.2720(3)		S(1)-C(2)-N(3)	110.3(2)	C(10)-C(11)-C(17)	109.9(2)
C(19)	0.5758(2) 0.6496(2)	0.0597(3)	0.1538(3)	0.050(1)	S(1)-C(2)-N(6)	135.8(2)	C(12)-C(11)-C(13)	110.1(2)
C(20) C(21)	0.0490(2)	0.0753(3) 0.1322(3)	0.1129(3) 0.1931(3)	0.053(1) 0.045(1)	N(3)-C(2)-N(6)	113.8(2)	C(12)-C(11)-C(17)	112.0(2)
, ,		, ,	` '	0.045(1)	C(2)-N(3)-C(8)	106.2(3)	C(13)-C(11)-C(17)	109.3(3)
C(22)	0.7382(2)	0.1738(3)	0.3101(3)		C(2)-N(3)-C(4)	115.4(2)	C(5)-C(12)-C(11)	111.2(2)
C(23)	0.6633(2)	0.1589(3)	0.3498(3)	0.044(1)	C(4)-N(3)-C(8)	138.1(2)	C(11)-C(13)-C(14)	113.3(3)
Cl(24)	0.82499(6)	0.15202(9)	0.1428(1)	0.0651(4) 0.045	N(3)-C(4)-C(5)	111.4(3)	C(13)-C(14)-C(15)	110.2(3)
H(8)	0.5276	0.1970	0.4731	0.043	N(3)-C(4)-C(9)	123.3(2)	C(14)-C(15)-C(16)	109.8(3)
H(9a)	0.4176	0.1839 0.2918	0.6385 0.5537	0.050	C(5)-C(4)-C(9)	125.3(3)	C(15)-C(16)-C(17)	111.3(3)
H(9b)	0.3593 0.2919	0.2918	0.5557	0.030	S(1)-C(5)-C(4)	112.9(3)	C(11)-C(17)-C(16)	113.9(2)
H(10a)			0.6779	0.049	S(1)-C(5)-C(12)	122.8(2)	C(7)-C(18)-C(19)	120.9(2)
H(10b)	0.2868 0.1132	0.2560 0.0902	0.3720	0.049	C(4)-C(5)-C(12)	124.3(3)	C(7)-C(18)-C(23)	121.1(3)
H(12a) H(12b)	0.1132	0.0902	0.3720	0.046	C(2)-N(6)-C(7)	103.5(2)	C(19)-C(18)-C(23)	118.0(3)
H(13a)	0.1038	0.2346	0.4883	0.040	N(6)-C(7)-C(8)	111.0(3)	C(18)-C(19)-C(20)	121.8(3)
	0.1293	0.2340	0.6431	0.051	N(6)-C(7)-C(18)	120.6(3)	C(19)-C(20)-C(21)	118.3(3)
H(13b)			0.5763	0.051	C(8)-C(7)-C(18)	128.3(3)	C(20)-C(21)-C(22)	121.8(3)
H(14a)	-0.0283 -0.0091	0.1853 0.1315	0.3703	0.053	N(3)-C(8)-C(7)	105.4(2)	C(20)-C(21)-C1(24)	118.8(3)
H(14b)				0.055	C(4)-C(9)-C(10)	108.7(2)	C(22)-C(21)-C1(24)	119.4(2)
H(15a)	-0.0705	0.3303	0.4130 0.5305	0.060	C(9)-C(10)-C(11)	114.4(3)	C(21)-C(22)-C(23)	119.5(3)
H(15b)	0.0123 0.0345	0.3820 0.2752	0.3303	0.000	C(10)-C(11)-C(12)	108.1(2)	C(18)-C(23)-C(22)	120.7(3)
H(16a)								
H(16b)	0.0465	0.4164	0.3510	0.057				
H(17a)	0.1804 0.1934	0.3790 0.3154	0.5248 0.4086	0.048 0.048				1 /0 **
H(17b)				0.048			which they are attached	
H(19)	0.5198	0.0188	0.0997	0.058	0.96 Å), 1973 corrected reflections with $F_0 > sd(F_0)$, weights $w =$			
H(20)	0.6450	0.0474	0.0308	0.000	$1/(s^2(F_0) + 0.0002 \cdot F_0^2)$, and 219 varied parameters. Final R = 0.042			

corrected for LP but not for absorption (m = 3.34 cm⁻¹), were merged to 3082 unique non-extinct reflections ($R_{merge} = 0.04$ on F). The structure was solved by direct methods using the XTAL3.1 suite of programs [10]. In the subsequent preliminary structure refinement it turned out that the crystal used for data collection was a pseudo-merohedral twin with an approximate volume ratio of 9:1 and with practically perfect superposition of h,k,l and -h,l,k,l reflections for the two twin components (R value about 0.12). After optimization calculations the twin volume ratio was found to be close to 78:12 and the structure factors were corrected according to $F_{corr} = F_o \cdot ((l-x) \cdot F_{c(hkl)}^2/((l-x) \cdot F_{c(h-lkl)}^2))$, x = 0.12. The final structure refinement was carried out with program SHELX76 [11] using anisotropic temperature factors for non-hydrogen atoms, hydrogen atoms with isotropic temperature factors in idealized

0.2129

0.1882

0.3643

0.4317

0.053

0.052

0.7951

0.6685

H(22)

H(23)

positions riding with the atom to which they are attached (C-H = 0.96 Å), 1973 corrected reflections with $F_o > sd(F_o)$, weights w = $l/(s^2(F_o) + 0.0002 \cdot F_o^2)$, and 219 varied parameters. Final R = 0.042 and wR = 0.044. Parameter for extinction correction was 0.0016(3). Maximum shift/s in final l.s. cycle < 0.01. Minimum and maximum difference electron densities were -0.233 and 0.24 e $A^{0.3}$ [12].

Synthesis of 2,3, 4a-4c, 5a-5c from Spiro[5.5]undecan-3-one.

4,7-Dihydrospiro[benzo[d]thiazole-6(5H), 1'-cyclohexane]-2-amine 3.

A mixture spiro[5.5]undecane-3-one 1 (1.40 g 8.43 mmoles), thiourea (1.28 g, 16.4 mmoles) and iodine (21.30 g, 8.43 mmoles) was reacted for 24 hours at 100°. After the reaction was completed, the resulting mixture is cooled to ambient temperature, washed with 10 ml of diethyl ether and filtrated. The crude product was recrystallized first from water then from diethyl ether. Yellow crystals of 2 (2-70 g, 92%) were obtained, mp 150-152°; ¹H nmr: d 1.10-1.53 (10H, in, Cyclohexane-H), 1.62 (2H, t, 5-H, J = 5.3 Hz), 2.35 (2H, s, 7-H), 2.40 (2H, t, 4-H, J = 5.5Hz), 7.10 (1H, HI), 9.07 (2H, s, NH₂).

Compound 2 was dissolved in concentrated ammonia liquor and extracted with diethyl ether to give yellow a solid, 4,5-dihydrospiro[benzo[d]iazole-6(7H), 1'-cyclohexane]-2-amine 3 (1.60g, 93%), mp 50-52; 1H nmr: d 1.30-1.59 (10H, in, Cyclohexane-H), 1.68 (2H, t, 5-H, J = 5.3 Hz), 2.30 (2H, s, 7-H), 2.50 (2H, t, 4-H, J = 5.3 Hz), 4.80 (2H, b, NH₂); 13 C-nmr: d 21.8 (t, 2C, 3'-C, 5'-C), 22.9 (t), 26.5 (t), 29.2 (s, 6-C), 33.3 (t), 33.9 (t), 35.9 (t, 2C, 2'-C, 6'-C), 117.0 (s), 143.9 (s), 165.3 (s)

General Synthesis Procedure for 4a-4c from 3.

Spiroammothiazole 3 (1.32 mmoles) and bromomethyl (halo-)phenyl ketone (1.31 mmoles) were dissolved in a small amount of anhydrous benzene and stirred for 12 hours at ambient temperature. The reaction mixture was filtrated, washed and dried to give colorless crystals of 4a-4c respectively.

3-(2"-Oxo-2"-phenylethyl)-4,7-dihydrospiro[benzo[d]thia-zole-6(5H), 1'-cyclohexane-2(3H)-imme Hydrobromic Salt 4a.

Compound 4a was obtained in 57% yield, mp 155-157°; 1 H nmr: d 1.20-1-50 (10H, m, Cyclohexane-H), 1.60 (2H, t, 5-H, J = 5.4 Hz), 2.35 (2H, b, 4-H), 2.47 (2H, s, 7-H), 5.74 (2H, s, 1'-H), [7.65 (2H, dd, 3"-H, $J_1 = J_2 = 7.7$ Hz 5"-H), 7.80 (1H, dd, 4"'-H, $J_1 = J_2 = 7.7$ Hz), 8.80 (2H, d, 2"'-H, 6"'-H, $J_1 = 7.7$ Hz), Phenyl-H], [7.38 (1 H, s), 9.50 (1H, s, NH and HBr)].

3-(2"-Oxo-*p*-chlorophenylethyl)-4,7-dlhydrospiro[benzo[*d*]thiazo-6(5*H*), 1'-cyclohexane]-2(3*H*)-imine Hydrobromic Salt 4b.

Compound 4b was obtained in 56% yield, mp 159-161°, 1 H nmr: d 1,25-1.50 (10H, m, Cyclohexane-H), 1.60 (2H, b, 5-H), 2.32 (2H, b, 4-H), 2.48 (2H, s, 7-H), 5.79 (2H, s, 1'-H), 7.75 (2H, d, Phenyl-H, J = 8.6 Hz), 8.08 (2H, d, Phenyl-H, J = 8.6 Hz), 9.59 (2H, s, NH and HBr).

3-(2"-Oxo-*p*-bromophenylethyl)-4,7-dihydrospiro[benzo[*d*]thiazo-6(5*H*), 1'-cyclohexane]2(3*H*)-imine Hydrobromic Salt **4c**.

Compound **4c** was obtained in 52% yield, mp 160-162°; ${}^{1}\text{H}$ nmr: d 1.20-1.52 (10H, m, Cyclohexane-H), 1.60 (2H, t, J = 5.3 Hz, 5-H), 2.32 (2H, b, 4-H), 2.42 (2H, s, 7-H), 5.74 (2-H, s, 1"-H), 7.90 (2H, d, Phenyl-H, J = 7.7Hz,), 8.01 (2H, d, Phenyl-H, J = 7.7Hz), 9.52 (2H, s, NH and HBr).

General Synthesis Procedure of 5a-5c from 4a-4c.

Compound 4a (0.52 mmole) was dissolved in 50 ml of anhydrous ethanol, refluxed for 5 hours and neutralized with 10% potassium carbonate. The solid product which formed was filtrated, dried and recrystallized from ethanol to give colorless crystal 5a-5c.

2-Phenyl-5,8-dihydrospiro[imidazo[2,1-*b*]benzo[*d*jthiazo-7(6*H*), 1'-cyclohexane] **5a**.

Compound 5a was obtained in 50% yield, mp 123-124°.

Anal. Calcd. for $C_{20}H_{22}N_2S$: C, 74.49; H, 6.88; N, 8.69. Found: C, 74.27; H, 7.07; N, 8.47.

2-(p-Chlorophenyl)-5,8-dihydrospiro[imidazo[2,1-b]benzo[d]-thiazo-7(6H), 1'-cyclohexane 5b.

Compound 5b was obtained in 81% yield, mp 195-197°. Anal. Calcd. for $C_{20}H_{21}N_2SCl$: C, 67.30; H, 5.93; N, 7.85. Found C, 67.04; H, 5.73; N, 7.69.

2-(*p*-Bromophenyl)-5,8-dihydrospiro[imidazo[2,1-*b*]benzo[*d*]thi azo-7(6*H*), 1-cyclohexane **5c**.

Compound 5c was obtained in 100% yield, mp 211-213°. Anal. Calcd. for C₂₀H₂₁N₂SBr: C, 59.85; H, 5.27; N, 6.98; Br, 19.91. Found: C, 59.40; H, 5.30, N, 6.80; Br, 19.81.

REFERENCES AND NOTES

- [1] J. F. Cheng, Y. Ohizumi, M. R. Walchli, and H. Nakamura, J. Org. Chem., 53, 4621 (1988).
- [2] B. Refouvele, J. F. Robert, J. Couquele, and P. Tronche, *J. Heterocyclic Chem.*, **31**, 77 (1994).
- [3] S. C. Shilcrat, D. T, Hill, P. E, Bender, D. E. Griswold, P. W. Baures, D. S. Eggleston, I. Lantos, and L. N. Pridgen. *J. Heterocyclic Chem.*, **28**, 1181, (1995).
- [4] P. E. Bender, D. E. Griwold, M. DiMartmo, D. T. Walz, I. Lantos and C. B. Ladd, *J. Med. Chem.*, 28 1169 (1985).
- [5] L. Fisera, F. Sauter, J. Froelich, Y. Feng, and P. Ertl, Chem. Monthly, 125, 553 (1994).
- [6] L. Fisera, F. Sauter, J. Froelich, Y. Feng, and K. Mereiter, *Chem. Monthly* **125**, 909 (1994).
- [7] J. Froelich, L. Fisera, F. Sauter, Y. Feng, and P. Ertl, *Chem. Monthly*, **126**, 75 (1995).
- [8] Y-Feng and X. Zhang, J. Tianjin Univ. (China), 29, 516(1996).
- [9] A. Singh, J. Mohan and H. K. Pujari, *Indian J. Chem.*, **14b**, 997 (1976).
- [10] S. R. Hall, and R. F. Stewart, editors: XTAL3.1 reference manual. Universities of Western Australia, Australia, and Maryland, 1154, 1990.
- [11] G. M. Sheldrick,: SHELX76. Program for Crystal Structure Determination. University of Cambridge, England, 1976.
- [12] R. C. G, Killean, J. L. Lawrence, J. U. Cameron, and A. Sharma Acta Cryst. B31, 1217 (1975).